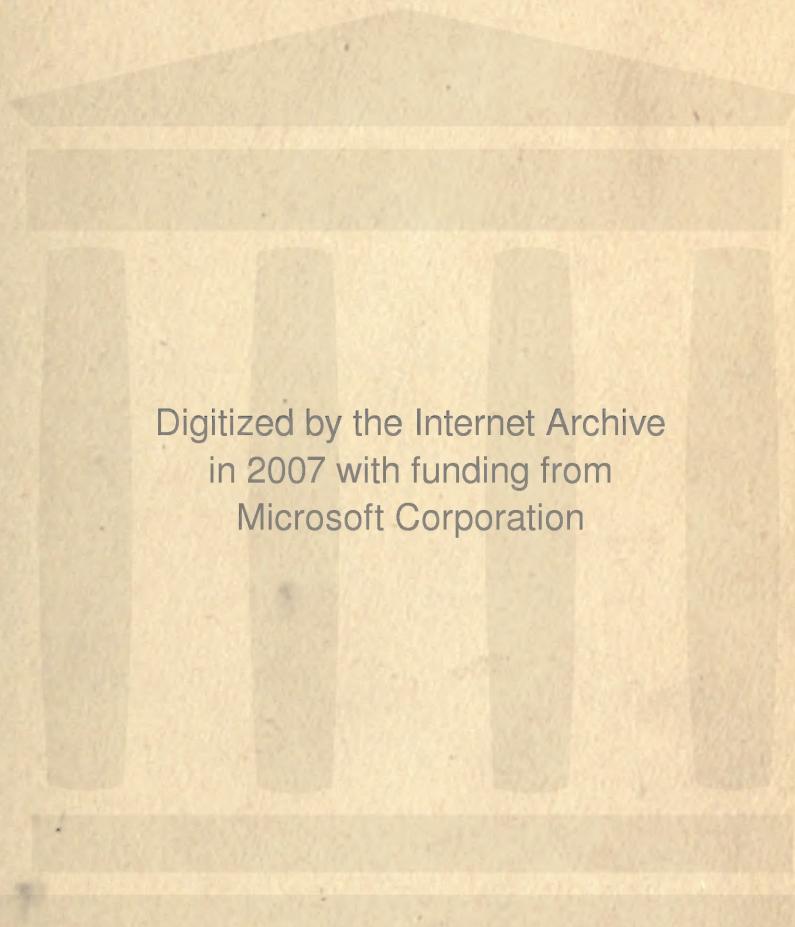


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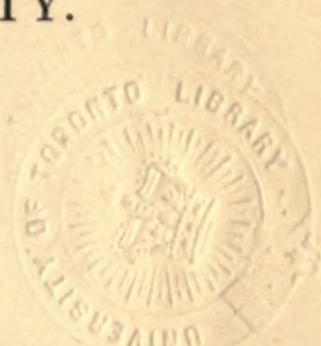


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THE PHYSICAL SOCIETY OF LONDON
AND
THE OPTICAL SOCIETY.



A *DISCUSSION*
ON
"THE MAKING OF REFLECTING
SURFACES,"

Held on 26th November, 1920

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16.11.26

AT THE

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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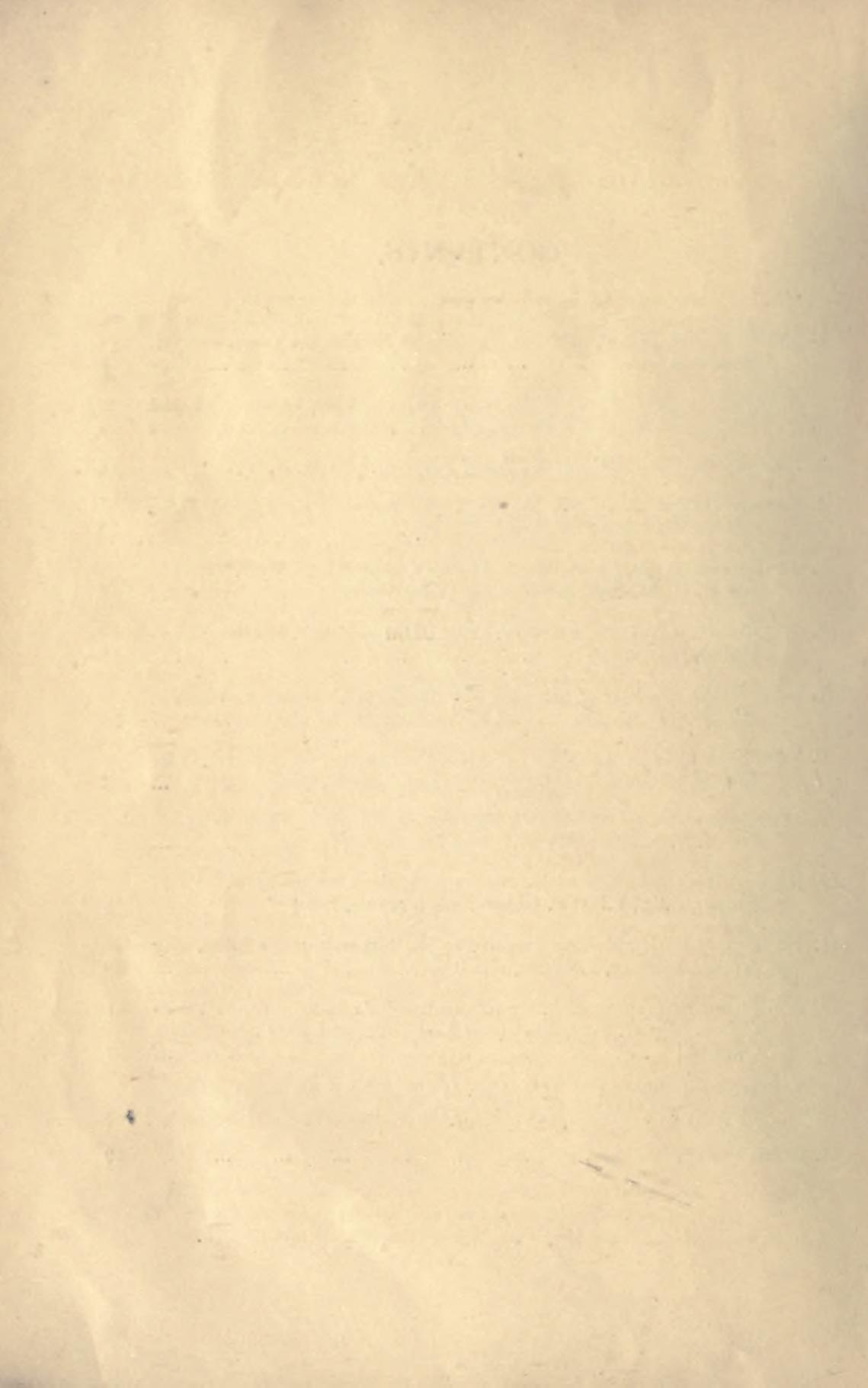
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1.—“SURVEY OF THE BIBLIOGRAPHY ON METALLIC DEPOSITION ON GLASS.”

By R. KANTHACK.

The bibliography of the subject may seem disappointingly small when ultimately submitted to you. As a matter of fact, I have discovered that the literature on the preparation of metallic films on glass is *enormous* if one includes every available reference, but that it is comparatively small if one eliminates that endless mass of repetition, abstracts, merest notices which are to be found in a dozen contemporaries, and the recorded successes and failures of amateurs. I have been forced to eliminate hundreds of empty references, but I have neither recorded nor eliminated anything that I have not been able to verify at the source.

While preparing this bibliography, or so much of it as I have so far been able to compile, I have endeavoured to keep before me what to me seems the ultimate object of such a bibliography, viz., to furnish a starting point for the methodical study of the fundamental principles of metallic deposition on glass and to establish a chemical and physical working basis for the development of unerring processes. I have tried, therefore, to discern how much of what has been published is scientific, how much is recipe work pure and simple, and how much is useless ballast. I have been on the look-out for anything that might suggest material for scientific investigation, but I fear I shall have little to offer.

When in 1835 LIEBIG wrote in the “Annalen” that when aldehyde is mixed with silver oxide and water and then heated the silver at once becomes reduced and is deposited on the sides of the test-tube in the form of a brilliant mirror, and that there was no evolution of gas, he made a scientific announcement of fundamental importance.

From 1843 onwards (if we ignore the earlier attempts of Count Rumford with essential oils) process upon process has been devised and described in an endless chain of variation. Fundamentally most of these processes have sprung from Liebig’s discovery, and the bulk of the literature which I have been able to collect is made up of recipes and working directions, nothing more or less.

DRAYTON stands at the head of this list with his patent of 1843, in which the reducing agent was composed of alcohol and oil of cassia. (May I remind you that cassia oil contains an aldehyde group?) His invention proved a failure in practice, because his mirrors became spotted in time. In 1848 he modified his process, using grape sugar and alcohol in the reducing fluid and working at 160°F.

In 1845 an anonymous writer in the “Mechanics’ Magazine” described a working application of a method ascribed to FARADAY, where wood naphtha and oils of cassia and cloves figure in the reducing solution.

BOETTGER’s process, with cassia oil, oil of cloves and alcohol in the reducing fluid, was likewise published in 1845.

In 1849 VOHL recommended guncotton dissolved in caustic potash as the reducing agent, and this process seems to have been much used in Germany for scientific purposes.

In 1855 PETITJEAN took out a patent for silvering, gilding and platinising glass, in which tartaric acid occurred as the reducing agent. His process met with much favour and seems to have been a commercial success.

LIEBIG published the results of the experiments which he undertook at the invitation of Prof. Steinheil in 1856. His formula included silver nitrate, caustic potash (or soda), and sugar of milk.

When we refer to Liebig as the scientific originator of the process of silvering by chemical deposition we do not associate him with silvering as an industry ; yet, from the letters published by LENK five years ago, it appears that he not only took a lively interest in the manufacture of mirrors during the period 1859-1864, but also that his practical share in a mirror factory occasioned him much worry, and he seems to have had a hard fight against Petitjean. In 1862 Liebig communicated to Craemer his latest working formula, which differed considerably from that of 1856. The silver solution was prepared with caustic soda and ammonium carbonate (or sulphate), and the reducing fluid contained sugar candy, tartaric acid, and copper sulphate.

In 1861 CIMEG took out a patent for a Rochelle salt process, and part of this process consisted in washing the glass, before silvering, with a weak solution of Rochelle salt.

In 1863 MARTIN published in the "Comptes Rendus" a formula composed of silver nitrate, nitrate of ammonia, caustic potash, alcohol, sugar candy and tartaric acid. In the course of years this process reappeared in various modified forms. PIAZZI SMITH, for example, gives details of BELL'S modification in the "Brit. Journal Photographic Almanac" of 1881. In this paper he has some uncomplimentary remarks for what he calls Liebig's "milk-and-water" films. A full description of Martin's method is also given in Eder's "Photographisches Jahrbuch" for 1887.

DRAPER described very fully in "The Smithsonian Contributions for 1864" a process of silvering by a development of Cimeg's method with elaborate directions for cleaning, silvering, and polishing.

The KRIPPENDORF-BOETTGER-BOTHE process of 1871 is also a development of Cimeg's method.

BURTON worked out a silver nitrate, caustic potash, loaf sugar and alcohol formula in 1873.

R. SIEMENS used aldehyde-ammonia as a reducing agent, washing the glass first with carbonate of potash.

PRATT patented a method in 1876 which included an interesting feature, in that he rubbed the glass, before silvering, with protochloride of tin mixed with ammonium oxalate and putty powder and then washed it with a solution of ammonium oxalate, grape sugar, lime, and potassium cyanide. In a paper read before the Fifth International Congress of Applied Chemistry in 1903 by M. TOCH, in which he professes to reflect the last word in silvering as practised in America, the preparation of the glass with stannous chloride and stannic oxide (*i.e.*, putty powder) figures very prominently ; and R. NAMIAS suggested in 1897 that these bodies enter into molecular combination with the silica of the glass and create favourable conditions for metallic deposition by forming a tin silicate. Others have suggested catalysis, which, as you know, is a favourite theory with mystified chemists.

In 1876 LENOIR, of gas-engine fame, invented a process by which the silver deposited on the glass was partly converted into amalgam by being bathed with mercurio-potassium cyanide, when a partial exchange of the metals takes place. The object was to obviate the yellow tint to which silver mirrors were liable.

Perhaps it was also an attempted resuscitation of an old industry without its devastating effects on health.

In this connection I may mention a paper by JOLLES and WILD (1891) on the origin and prevention of brown spots. They ascribe these to the formation of sulphide of silver by free sulphur, which is formed by the reduction of the original sodium sulphate of the glass under the influence of the hot furnace gases. Glass should therefore be silvered immediately after manufacture ; but, if free sulphur has formed during storage, it should be boiled in a 10 per cent. solution of sodium carbonate.

BOETTGER, in 1877, advocated the use of guncotton dissolved in caustic soda. You will remember that in principle he was anticipated by Vohl in 1849.

In 1880 BRASHEAR published his well-known and widely used process, which is a modification of Burton's. His method has been further improved by WADSWORTH, who gives in the "Astrophysical Journal" for 1895 a very full description and working directions with quantitative data for the silvering of specula.

PALMIERI's glycerine process was described in 1887 in the "Gazzetta chimica italiana." His paper contains a table showing the effects of temperature, time, and the composition of the reducing agent.

LUMIÈRE's process was published in 1895. This process appears to have worked well in many hands ; but it is subtle, the difficulty being to hit off the right proportion of formaldehyde.

M. IZARN has therefore described a modified method with full details in the "Comptes Rendus" for 1902 ; and a precise interpretation and development of the method has been given by EVERITT in the "Brit. Journ. of Photography" for 1903.

There is also a notable paper on silvering by SCHMIDT in the "Photographische Mitteilungen" for 1901, where he describes and criticises Lumière's method, and describes and recommends more particularly Liebig's method, Krippendorf's combined Boettger-Bothe process, and the Martin process.

In Wood's method of 1896 the reducing agent is dextrose.

The silvering and gilding process by *spraying* from two independently adjustable jets, as patented by the IMPROVED ELECTRIC LAMP Co., does not appear to have been a success from the point of view of the flat-surface operator, judging from what little I have been able to read about it.

RITCHIEY's paper in the "Smithsonian Contributions" of 1904 is important to those who are called upon to silver large specula, and the same applies to the various well-known writings of Common, Browning, Thorntwaite, and others.

In a German patent specification describing the process of the HEYDEN COMPANY, of Radebeul, near Dresden, the following are pointed out as the main drawbacks of existing processes : great skill is needed ; failure occurs frequently ; silver is precipitated as soon as the solutions are brought into contact ; a small portion only is deposited on the glass surfaces, whilst the greater portion has to be converted back into silver nitrate. The specification declares separate spraying to have proved a failure. The Radebeul method consists in wetting the glass with a silver nitrate solution containing formaldehyde and glycerine (or other reducing agents). This is rubbed on the surface, the latter is then wetted with a suitable quantity of the solution, the plate turned into a vertical position, and the wet plate exposed to ammonia vapour over a floor covered with liquid ammonia, or dipped into a solution of ammonia in benzole or other fluid which is not miscible with aqueous solutions. The mirror is said to form instantaneously.

I have come across one book only which deals exclusively with the manufacture of mirrors. This is FERDINAND CREMER's little book entitled "*Die Fabrikation der Silber-und Quecksilberspiegel*," published in 1888. It describes some 25 processes, including gilding and platinising, but there are no references to original sources, and it says little on the all-important manipulative side.

In this review I have not attempted to refer to the many resumés given in encyclopaedias and technological manuals, though some of these are very helpful.

There are a number of processes for gilding and platinising by Petitjean, Liebig, Draper, Bottler, Herrmann, Vasserot, Johnson, Dodé, van Aubel, and many others, to say nothing of some 50 patent specifications and scattered papers which I have not had time to consult. Many of these processes require furnace heat. There is, however, a process for platin-silvering in the cold which forms the subject of Rost's German patent of 1894.

On the subject of *nickeling glass reflectors* for celestial photography Wood has published an interesting article in the "*Astrophysical Journal*" of 1911. In this case the nickel is deposited electrolytically upon a film of silver.

I will now conclude by briefly referring to the more or less fundamental work which has been done to elucidate the *raison d'être* of metallic deposition.

The first scientific effort is LIEBIG's discovery of 1835, and when one remembers that there is an aldehyde group in many simple sugars and in some of the essential oils, that glycerol contains glyceraldehyde as a constituent, and so forth, Liebig's discovery would seem to extend over a wider field than appears at first sight.

SHENSTONE did something in 1845 to add greatly to the list of reducing agents.

In 1857 FARADAY transferred films of metal upon glass plates by deflagrating the metals with a Leyden battery. The film so obtained was far from uniform and lacked cohesion.

QUINCKE's paper in the "*Poggendorff's Ann.*" of 1866 details his experience in the making of metallic films and presents a few scientific aspects of interest.

In 1877 A. W. WRIGHT published in the "*Amer. Journal of Science*" a paper on the production of metallic films by electrical discharges in exhausted tubes. This method produces firm and uniformly thick deposits on plane glass.

PIAZZI SMITH's paper contains suggestions respecting the why and wherefore of the downward deposition and upward transference of the reduced silver.

ÖBERBECK, in his paper in the "*Annalen der Physik*" 46 (1892) on the behaviour of allotropic silver with respect to the electric current, has shown that the electrical resistance of silver films is very high immediately after deposition but continually diminishes with time. In one case the resistance declined from 144.5 ohms to 12.7 ohms in 140 days and was 10.9 ohms after 508 days. The minimum had not been reached in two years, but it was then very near that of solid silver.

An interesting paper on the chemistry of silvering is one by R. NAMIAS published in "*L'Industria*," of 1897, on silvered mirrors, wherein he sets up a chemical reaction theory to the effect that in the Rochelle salt process the double tartrate is changed into the double tartronate, from which he concludes that the proportions of the silver nitrate and Rochelle salt should be 680 to 282. He further concludes that the silver nitrate should be divided between the Rochelle salt and the ammoniacal solution. I have already referred to his suggestion respecting the part played by stannous and stannic compounds in the process of preliminary cleaning.

SCHMIDT (in the paper already mentioned) gives a scientific exposition of the meaning of "chemical," or, shall we say, "molecular," cleanliness.

VIGNON, writing in the "Bulletin de la Soc. chim." of 1903, has shown that a small percentage of copper facilitates deposition of silver by lowering the required working temperature. You will remember that copper figured in Liebig's later formula.

HERRMANN (in 1906) described a gilding process which may be suggestive to the investigator. He produces a primary invisible film by a mixture of gold chloride, an alkaline solution, and alcohol (the latter as a mild reducing agent). Once established, this primary film can readily be reinforced by a secondary visible coating. This process is interesting only, I should think, as a possible vehicle of further research.

CHATTAWAY's paper in the "Proc. of the Royal Society" of 1907 on "Copper Mirrors" is exceedingly suggestive. His reducing agent is phenylhydrazin, and his experiments have enabled him to formulate the reaction and to suggest a theory.

The most comprehensive scientific investigation on the subject which has probably ever been attempted is that undertaken by V. KOHLSCHÜTTER in conjunction with EMILIE FISCHMANN, an account of which covers no less than 49 pages of "Liebig's Annalen" of 1912.

Finally, we come to SILVERMANN and NECKERMAN's paper in the "Transactions of the Amer. Ceramic Society" of 1915, where a table is given showing the behaviour of various reducing agents, viz., Rochelle salt, formaldehyde, tartaric acid, citric acid, dextrin, tannin, sodium tartrate, milk sugar, stannous chloride, cane sugar, phenylhydrazin, formic acid, potassium nitrite, sodium sulphite, nitrous acid, ferrous sulphate, acetaldehyde. The object of their investigation in their own words is, "a thorough and systematic qualitative and quantitative study of methods for the precipitation of metals in mirror form from solutions of their salts." These investigations have not been concluded, so far as I know.

I will conclude my remarks by reading you a passage from Piazzi Smith's paper of 1881, from which it would seem that the Astronomer Royal of Scotland had a grievance. He says:—

"Then between and amongst all these methods—the Burton, the Martin, the Bell, and the Perry, together with the many points whereon they consent to agree with each other, but combine to differ *toto caelo* from the primitive milk-sugar and its mere milk-and-water sort of films, you might think a definite practical step of advance had been accomplished that would be patent to all men, denied by none, and would never be forgotten or removed by any.

"But, no! For it came to pass only a year ago that certain great administrative authorities in England, together with some heads of university science in Scotland, took upon themselves to ignore all the recent improvers, with their several improvements, and issue their orders to a certain astronomer to silver his observatory mirror on the most ancient and condemned plan of all. And when he explained and demonstrated that it was not the method by which the best film could be obtained, it was silvered for him over his head on that method precisely; and with what result? Simply this—that no man has seen either planet or star reflected in that speculum since then!"

I have not read this passage merely to amuse you. Six weeks of bibliography-hunting have given me the impression that at the present time—85 years after Liebig's classical discovery!—we have not evolved any method of chemical deposition on glass so scientific and practically perfect that it could be adopted officially. I think our gratitude is due to those who have convened this meeting as a first step towards a scientific solution of the problem.

2.—“A BIBLIOGRAPHY OF THE MORE IMPORTANT PAPERS ON THE CONSTRUCTION AND NATURE OF REFLECTING SURFACES.”

By R. KANTHACK.

1798.

S. BERNARD.—Description de la manière dont se polissent et s'étament les glaces coulées dans l'atelier au faubourg Antoine, *J. de l'École Polytechnique*, tome 2, cah. 5 (1798), 71-81.
 Translation: Description of the manner of polishing and silvering Plates for Looking Glasses (cast at St. Gobin) at the Manufactory in the Faubourg St. Antoine, Paris, The Repertory of Arts and Manufacture, 10 (1799), 351-358, 405-415.

1812.

VÉRÉA.—*Bull. Soc. d'Encour. ind. nat.* 12 (1812), 188. Also “On the composition for tinning the glass of mirrors,” *Repertory of Arts, Manuf. and Agric.*, ii., 25 (1814), 242.

1815.

THIELE.—*Beschreibung der Spiegelfabrik im Königl. Grossbritannisch-Hannoverschen Amte Nienover, Allgem. Handl. Ztg.*, Nürnberg (1815), 652-653. (Full description of making mirrors from rough cast plates and silvering by the amalgam process).

1824.

F. LANCELLOTTI.—*Sopra una nuova amalgama per la costruzione degli sphechi*, “*Giorn. di Fisica, chim., &c.* (Pavia), (ii.) 7 (1824), 132.

1832.

Editorial.—*Kunst- u. Gewerbe-B1.* 10 (1832), 85-92, *Reisebemerkungen über die Fabrikation der gegossenen Spiegel.* (Full description of grinding, polishing and amalgamation.)

1835.

J. v. LIEBIG.—“Ueber die Produkte der Oxydation des Alkohols, Aldehyd,” *Ann. d. Pharm.*, 14 (1835), 134-144. (Historical basis of modern silvering.)

1838.

OLIVIER.—Hoyau's mirror grinding machines, *Bull. Soc. d'Encour.* (1838), 155; also German in *Dingl. Polyt. J.*, 70 (1838), 4-22.

1843.

THOMAS DRAYTON.—Silvering glass for mirrors. *Brit. Pat. Spec.* 9,968/1,843.

1845.

J. STENHOUSE.—On some of the substances which reduce oxide of silver and precipitate it on glass in the form of a metallic mirror, “*Phil. Mag.*,” 26 (1845), 233-234.

“M” (anon).—New process of silvering glass, “*Mechanics' Mag.*,” 43 (1845), 190. (Particulars of Faraday's process.)

R. BOETTGER.—Silber, anstatt des Amalgambelegs zur Spiegelbereitung, “*Arch. d. Pharm.*,” 91 (ii., 41) (1845), 36-37.

MEURER.—Ueber das Versilbern des Glases behufs der Spiegelfabrikation, “*Dingl. Polyt. J.*,” 98 (1845), 293.

STEINHEIL.—Beschreibung einer Fabrikationsmethode genauer und nicht oxydirbarer Metallspiegel, “*Kunst- u. Gew. B1.*,” 23 (1845), 757-762. (Electrolytic gilding of metallic mirror surfaces and copper copying process); also “*Dingl. Polyt. J.*,” 99 (1846), 397.

1847.

LÜDERSDORFF.—Das Platiniren von Glas (zu Spiegeln), Porzellan, Steingut, &c., “*Verh. d. Ver. z. Beförder. d. Gewerbe*,” in Preussen, 1847, No. 2; also “*Dingl. Polyt. J.*,” 105 (1847), 36-41.

1848.

THOMAS DRAYTON.—Silvering glass, *Brit. Pat. Spec.* No. 12,358/1848. (Modification of formula of 1843.)

P. FLAMM.—Ueber die belgische Spiegelschleiferei, “*Kunst- u. Gew. B1.*,” 26 (1848), 498-505.

1849.

VOHLL.—“*Ann. d. Chem. u. Pharm.*,” 70 (1849), 840; “*Jahresber. üb. d. Fortschr. d. rein., pharm., u. techn. Ch.*” (Liebig u. Kopp) (1849), 473.

1851.

H. WEICKERT.—Neue Methode Glas zu versilbern, “ Polyt. Notizbl.” 6 (1851), 61-62; also “ Dingl. Pol. J.” 119 (1851), 362-363.

1855.

L. L. HILL.—Silvering glass. Brit. Pat. Spec. No. 1,093/1855. (Mannite and “ acidulated sugar” process.)

TONY PETITJEAN.—Silvering, gilding and platinising. Brit. Pat. Spec. No. 1,681/1855.

✓ M. FARADAY.—Petitjean’s process for silvering glass, “ Mech. Mag.” 65 (1856), 4-5.

J. V. LIEBIG.—Ueber Versilberung und Vergoldung von Glas, “ Ann. d. Ch. u. Pharm.” 98 (1856), 132-139; also “ Dingl. Pol. J.” 140 (1856), 199-204.

J. LÖWE.—Ueber die nasse Versilberung des Glases auf kaltem Wege, “ Dingl. Pol. J.” 140 (iii, 40) (1856), 204-206.

STEINHEIL.—Note on first silvered telescope mirror, “ Augsburger Allg. Ztg.” No. 84, 24, 3, 1856.

1857.

LÉON J. B. FOUCAULT.—Sur un nouveau télescope en verre argenté, “ C. R.” 44 (1857), 339-342.

Mémoire sur la construction des télescopes en verre argenté. (Extrait des “ Annales de l’Observatoire impérial de Paris,” t. v., 1858), in Recueil des Travaux scientifiques de Léon Foucault, Gauthier Billars, Paris, 1878, pp. 232-284.

BEEG.—Die Fürtner Spiegelfabrikation, “ Kunst-u. Gew. Bl.” 35 (1857), 610-623. (Detailed description of casting, grinding and polishing by machinery.)

M. FARADAY.—Experimental relation of gold (and other metals) to light, Phil. Trans., 147 (1857), 154.

1858.

C. F. VASSEROT.—Reflectors. Brit. Pat. Spec. No. 2,257/1858. (Palladium and platinum.)

R. WAGNER.—Glasversilberung, “ Dingl. Pol. J.” 148 (1858), 447.

1859.

J. S. BENSON.—Silvering glass. Brit. Pat. Spec. No. 438/1859.

E. R. H. UNGER.—Silvering glass and porcelain, “ Chem. News,” 1 (1859-60), 300. (Suggestion for silvering with silver nitrate and tannin.)

1861.

JOHN CIMEG.—Silvering glass. Brit. Pat. Spec. No. 619/1861.

1862.

V. MEUNIER.—Une Industrie de Bienfaisance; L’Argenture des Glaces selon le procédé exploité par MM. H. Brossette et Cie., Paris, 1862. (Petitjean’s process.)

JOHN CIMEG.—Depositing silver and other metals on fabrics, &c. Brit. Pat. Spec. No. 2,314/1862.

H. VOGEL.—Ueber die Zustände, in denen das Silber bei der Reduktion seiner Salze auf nassem Wege auftritt, “ Monatsber. d. Berl. Akad.” (1862), 123-132; “ Pogg. Ann.” 117 (1862), 316-341.

1863.

A. MARTIN.—Sur un procédé d’argenture à froid du verre, par l’emploi du sucre interverti, “ C. R.” 56 (1863), 1044.

1864.

H. DRAPER.—On the construction of a silvered glass telescope, fifteen and a half inches in aperture, and its use in celestial photography, Smithsonian contrib. to “ Knowl.” 14 (1864), repr. *ibid.*, 34 (1904), No. 1,459, 40-43.

F. BOTHE.—Versilberung des Glases auf kaltem Wege, “ J. f. prakt. Ch.” 92 (1864), 191-193; repr. “ Dingl. Pol. J.” 173 (1864), 292-294.

R. BOETTGER.—Ueber Bothe’s neues Verfahren der Glasversilberung, “ Polyt. Notizbl.” 19 (1864), 300-301; “ Dingl. Pol. J.” 174 (1864), 84-85; Silberspiele auf Glas, “ J. f. prakt. Ch.” 92 (1864), 424-425. (Modification of Bothe’s process.)

C. FINCKH.—Ueber Glas-Versilberung, Gew. Bl. a. Württ (1864), 106-108.

A. M. DODÉ.—Brevet No. 62701/1864, 2 me sér., t. xc, xiii, 3, pp. 2-3. L’application du platinage à l’abtention des glaces et des miroirs.

1865.

E. REICHARDT.—Die Darstellung von Silberspiegeln, “ Dingl. Pol. J.” 176 (1865), 139-141.

Discussion on

1866.

JOHN BROWNING.—A description of the new telescopes with silvered specula; and instructions for adjusting and using them. London: Straker & Sons; also "Chem. News," 14 (1866), 214 (Martin's process.)

QUINCKE.—Erfahrungen über Herstellung von Metallspiegeln, "Phot. Arch.," 7 (1866), 423-429.

1867.

J. V. LIEBIG.—Versilberung von Glas, "Ann. d. Ch. u. Pharm.," V. Suppl. (1867), 257-260. (Liebig's modified formula with copper in reducing fluid.) Also "Dingl. Pol. J.," 187 (1868), 236-238.

1868.

A. MARTIN.—Argenture du verre par le sucre interverti, "Ann. de Ch. et de Phys.," (iv.), 15 (1868), 94-100; also "Dingl. Pol. J.," 191 (1869), 43-48.

R. BOETTGER.—Ueber eine Vereinfachung des von Herrn Wernicke erfundenen Verfahrens der Vergoldung des Glases, "Pol. Notizbl.," 23 (1868), 129-131; also "Dingl. Pol. J.," 188 (1868), 288-290.

W. WERNICKE.—Ueber Vergoldung des Glases zur Herstellung optischer Spiegel, "Pogg. Ann.," 133 (1868), 183; also "Dingl. Pol. J.," 188 (1868), 51-54.

A. M. DODÉ.—Brevet No. 62701/1868. Full account (vide 1864) loc. cit.

1869.

E. V. FÜRTENBACH.—Die in der Neuzeit zur Vergoldung und Versilberung des Glases auf nassem Wege angewandten Methoden, "Bayer. Ind. u. Gew. Bl.," 1 (1869), 51-54. (Wernicke's Boettger's simplification, Martin's process, Liebig's method, Boettger-Bothe's method.)

1870.

C. WIEDEMANN.—Platinised looking-glasses, "Chem. News," 21 (1870), 207. (Dodé's process.)

1871.

KRIPPENDORF.—Versilberung von Glas nach Bothe's Verfahren, "Phot. Arch.," 12 (1871), 22-25; also "Dingl. Pol. J.," 200 (1871), 484-487.

1873.

H. J. BURTON.—Silvering on glass surfaces, "The Brit. J. Pht. Almanac," 1877, 89-90.

R. SIEMENS.—Silvering on glass, "Arch. d. Pharm.," 200 (1873), 233; also "Dingl. Pol. J.," 206 (1873), 419.

1876.

H. J. BURTON.—Further remarks on the silvering of plane mirrors and the subsequent treatment of the same, "Brit. J. Phot. Almanac," 1876, 58-60.

J. E. PRATT.—Silvering mirrors. Brit. Pat. Spec. No. 1,258/1876. (Rocking table.)

J. E. PRATT.—Preparing glass for silvering. Brit. Pat. Spec. No. 1,259/1876.

HIMLY.—Method of silvering, "Jahresber. d. physik. Ver. zu Frankfurt a/M.," 1876-1877, p. 19.

DEBRAY.—Sur le procédé d'amalgamation des glaces argentées de M. Lenoir, "Bull." de la Soc. d'Encour. ind. nat.," 75 (iii., 3) (1876), 19-22.

1877.

R. BOETTGER.—Ueber eine Verwendung der Schiesswolle zur Versilberung, "Jahresber. d. phys. Ver. zu Frankfurt a/M.," 1877-78, 23. (Note on collodion as a reducing agent; anticipated by Vohl, 1849.)

A. W. WRIGHT.—On the production of metallic films by the electrical discharge in exhausted tubes, "Amer. J. Sc. and Arts," 113 (iii., 13), 49-55.

1880.

H. BRASHEAR.—Hints on silvering specula, &c., "Engl. Mech.," 31 (1880), 327.

THORNTNHWAITE.—Hints on Reflecting and Refracting Telescopes, London, 1880.

1881.

H. E. BENRATH.—Silvering on glass, "Orig. Industrie-Blätter," 18 (1881), April; "Jahresber. üb. d. Fortschr. d. chem. Technol.," 27 (N.F., 12) (1881), 472-476; "Abstr. Chem. Centrabl.," 12 (1884), 446.

PIAZZI SMITH.—Silvering the front of glass, "Brit. J. Phot. Almanac," 1881, 36-42.

SIR JOHN CONROY.—Some experiments on metallic reflexion (ii.), "Proc." Roy. Soc., 31 (1881), 486-500.

1882.

G. PALMIERI.—Sull'azione redattrice della glicerina sui sali d'argenti ed applicazione di siffatto fenomeno all'argentaturo del vetro, "Gazz. chim. ital.", 12 (1882), 206-209; "Abstr. J. Chem. Soc.", 42 (1882), 1256.

1884.

O. LOHSE.—Ueber Silber- und Platinspiegel, "Zts. f. Instr.", 4 (1884), 26-27; also Eder's "Jahrb. f. Phot.", 1 (1887), 167-172.

1886.

A. KUNDT.—Ueber Doppelbrechung des Lichtes in Metallschichten, welche durch Zerstäuben einer Kathode hergestellt sind, "Wied. Ann. d. Phys. u. Ch.", 263 (N.F. 27) (1886), 59-71.

1888.

E. VAN AUBEL.—Platinumspiegel, "Neueste Erfin. u. Erfahr.", 15 (1888), 318.

M. BORY.—Versilberungsverfahren für Spiegel, "Neueste Erfind. u. Erfahr.", 15 (1888), 160.

FERD. CREMER.—Die Fabrikation der Silber- und Quecksilberspiegel, oder das Belegen der Spiegel auf chemischem und mechanischem Wege, A. Hartleben's Verl., Vienna, Budapest, Leipzig, 1898.

O. LEHMANN. "Molecularphysik," Vol. I., pp. 581 and 849, Leipzig, 1888.

1889.

M. CAREY LEA.—On allotropic forms of silver, "Am. J. Sc.", 37 (1889), 476-491.

M. CAREY LEA.—The properties of allotropic silver, "Am. J. Sc.", 38 (1889), 237-241.

1890.

R. KAYSER.—Die Herstellung von mit Silber belegten Spiegeln, "Zts. f. angew. Chem." (1890), 541-542.

1891.

A. JOLLES and E. WILD.—Ueber die Entstehung der braunen Flecken und der Vermeidung derselben bei Spiegelfabrikation, "Zts. f. angew. Ch.", 4 (1891), 266-268.

1892.

A. OBERBECK.—Ueber das Verhalten allotropen Silbers gegen den elektrischen Strom, "Ann. d. Phys. u. Ch.", 48 (1892), 265-280.

A. A. COMMON.—"The Observatory," (1892), No. 193.

H. LÜDTKE.—Ueber die Eigenschaften verschiedener Silbermodificationen, "Wied. Ann. d. Phys. u. Ch.", 283 (N.F. 50) (1893), 678-695.

A. ROST.—Verfahren zur Herstellung eines platin- und silberhaltigen Spiegelbelags, D.R.P. No. 77,725/1894.

1893.

AUG. and LOUIS LUMIÈRE.—Argenture des glaces à froid, "J. de Phys., iii., 4 (1895), 29-30.

F. L. O. WADSWORTH.—Notes on silvering solutions and silvering, "Astro. phys. J.", 1 (1895), 252; orig. "Zts. f. Instr.", 15 (1895), 22-27.

1896.

J. T. WOOD.—A method of silvering glass, "J. Soc. Chem. Ind.", 15 (1896), 19; "Engl. Mech.", 59 (1884), 85.

A. A. COMMON.—Silvering glass mirrors, appendix to "Optical instruments and silvering glass surfaces," "Proc. Roy. Artill. Inst.", 23 (1896), No. 9.

E. EDSER and H. STANSFIELD.—Phase-changes of light on reflection at a silvered surface, "Nature," 56 (1897), 504.

R. NAMIAS.—Sull'industria degli specchi argentati, "L'Industria," 11 (1897), 734-736.

1898.

S. COPPER-COLES.—An electrolytic process for the manufacture of parabolic reflectors, "Electrician," 40 (1897-8), 583-586.

BOTTLER.—Praktische Erfahrungen über Versilberung und Vergoldung von Glas, "Neueste Erfind. u. Erfahr.", 25 (1898), 145-148.

F. FAFET.—Industrie des miroirs argentés, "Rev. de chim. ind.", 9 (1898), 5-8. (See R. Namias.)

IMPROVED ELECTRIC LIGHT CO. (London).—Brit. Pat. Spec. No. 9,977/1898. Application of silvering or gilding solutions to glass, porcelain, &c. (Spraying from double jet.)

1899.

EDEL.—Darstellung von Silberspiegeln nach Edel, "Deut. Chem. Ztg." (1898), 36; also "Bayer. Ind. u. Gew. Bl.", 31 (1899), 48.

Discussion on

1900.

DR. WEISKOPF & Co.—Process for making copper mirrors. D.R.P. No. 124,710/29.4.1900.

1901.

H. SCHMIDT.—Die Herstellung von Silberspiegeln, "Photogr. Mitt.", 38 (1901), 109-111, 117-120.

C. LAVAL.—Process of preparing silvering liquid. U.S. Pat. No. 670,156/19.3.1901.

1902.

C. ROST.—Herstellung von parabolischen Reflektoren für Scheinwerfer auf elektrolytischem Wege, "Elektroch. Ztg.", 8 (1902), 263-272.

IZARN.—Silvering by Lumière's formol method. C.R., 135 (1902), 240-242.

1903.

P. EVERITT.—Silvering mirrors. "Brit. J. Phot.", 50 (1903), 25-26.

L. VIGNON.—Influence du cuivre dans l'argenture du verre, "Bull." Soc. Chim. (iii., 29) (1903), 515-517.

M. TOCH.—The Art and Science of Silvering Mirrors, 5th Intern. Congress for Appl. Chem., Berlin, Vol II. (1903), 676-682.

G. W. RITCHIE.—On the Modern Reflecting Telescope and the Making and Testing of Optical Mirrors, Smithson. contrib. to "Knowl.", 34 (1904), No. 1,459, 40-43.

1907.

CHEM. FABRIK VON HEYDEN AKT.-GES., in Radebeul, near Dresden, Verspiegelungsverfahren, D.R.P. 199,503/19.7.1907.

1908.

F. D. CHATTAWAY.—Copper mirrors, "Proc." Roy. Soc., Lond., 80A (1907), 88-92; "Chem. News," 97 (1908), 19-21.

1909.

A. PEROT.—Sur un mode de protection de l'argenture des miroirs, "C. R.", 149 (1909), 725.

1910.

O. HAUSER and E. BIESALSKI.—Einfache Herstellung von Metallsulfidspiegeln, "Chem. Ztg.", 34 (1910), 1079.

1911.

H. D. CURTIS.—Methods of silvering mirrors, "Publ. Astr. Soc. of the Pacif., San Francisco, Cal.", 23 (1911), 13-32 (with tables).

R. W. WOOD.—Nickeled glass reflectors for celestial photography, "Astrophysical J.", 34 (1911), 404-409.

1912.

E. C. C. BALY.—Spectroscopy (1912). Longmans, Green & Co., Appendix, pp. 650-653.

V. KOHLSCHÜTTER.—Ueber Bildungsformen des Silbers, "Lieb. Ann. d. Ch.", 387 (1912), 86-135.

1914.

E. SENIOR.—Silvering mirrors for photographic purposes, "Knowledge," 37 (1914), 402.

E. LENK.—Die Herstellung der Silberspiegel nach Liebig, from unpublished letters (1859-1864), "Zts. f. angew. Ch.", 28 (1914), i., 2-7, 12.

1915.

A. SILVERMANN and P. D. NECKERMANN.—The silvering of glass, "Trans. Am. Cer. Soc.", 17 (1915), 505-519.

3.—“NOTES ON THE FORMALDEHYDE PROCESS OF SILVERING.”

By H. N. IRVING.

Preparation of Standard Solutions.

(1) *Silver Nitrate Solution.*—Dissolve 1 drachm of pure nitrate of silver in 4 oz. of distilled water, and add liquid ammonia (sp. gr. 0.880) drop by drop until the solution is turned a muddy brown colour. Then add more ammonia until the solution has a slight colour, its appearance being like that of clean water to which a little milk has been added. This is very important, as the silver solution must not be over ammoniated. The solution is then ready for use.

(2) *Formaldehyde Solution.*—Mix from 8 to 10 drops of formaldehyde with 4 oz. of distilled water and keep for a day or so. It is important that the formaldehyde should be of the very best quality. The solution should be kept well corked, as otherwise its strength will vary.

To Silver Glass.—Clean the glass thoroughly with distilled water until the water clings all over its surface. Then drain off the water and mop well the surface with the silver nitrate solution, keeping the silver on for at least one minute. Mix about 1 part of the silver solution with 2 parts of the formaldehyde solution, and pour the mixture gently over the glass surface. Care should be taken that the liquid is kept in motion during the process of silvering, which should not take more than 2 minutes in a room at moderate temperature. Wash the specimen thoroughly with distilled water and stand it on edge to dry.

To Polish a Silvered Surface.—Make a pad of chamois leather, and go lightly over the silvered surface with it, using some fine washed rouge. The silver film should be hard, and should take on a brilliant black polish, which should with care last a number of years.

4.—“SOME WORKSHOP NOTES ON SILVERING.”

By JAMES WEIR FRENCH, D.Sc.

(Messrs. Barr & Stroud, Ltd., Glasgow.)

Many processes for the silvering of optical parts have been introduced from time to time, but the number in practical use is small. The best known processes are :—

- (1) The old Mercury Tin Amalgam process.
- (2) The Formaline process.
- (3) The Rochelle Salt process.
- (4) The Tartaric Acid process.
- (5) The Brashear process.

Numerous attempts to project under vacuum fine deposits of silver upon glass surfaces have been made, and I understand that the latest information on this subject is to be placed before the meeting. There appears to be little difficulty in producing small reflectors of 1 cm. or more in diameter. Hitherto it has been very difficult to produce large, uniformly reflecting surfaces by this method.

(1) MERCURY TIN AMALGAM PROCESS.

This process, the details of which are well known, has not been used regularly in commerce for many years, and it is now rarely used by opticians, although there are still some sea-going officers who favour it from the point of view of durability. The process has been abandoned in the industry in favour of the Rochelle salt process, because of the long time—several weeks—required for the removal of the excess mercury, and principally because of the danger to health. As the final surface contains about 20 per cent. of mercury, it is to be expected that the light-reflecting power is not good from the point of view of the optician.

There is a characteristic difference between the mercury tin amalgam and the precipitated silver in that the former cannot be used like the latter for surface silvering. The uniformity of the amalgam surface is dependent upon the polished surface of the glass with which it is in contact. The surface in contact with the glass appears highly reflecting, whereas the other side in contact with the air has a dull matt appearance. When, on the other hand, a thin layer of silver is deposited upon the polished surface of glass, both sides can be made highly reflecting.

(2) FORMALINE PROCESS.

This process has the sole merit of being very simple and rapid, and therefore suitable for experimental work, but in the present stage of its development it is rarely used in optical manufacturing. Compared with the Brashear and Rochelle salt surfaces, the formaline surface is dark. The process has the additional disadvantage that one deposit cannot be laid upon another, and the surface cannot be electrically plated with copper.

(3) ROCHELLE SALT PROCESS.

This process is very generally used in commerce and by opticians. It gives a brilliant reflecting surface, which, however, is about 5 per cent. or 6 per cent. less brilliant than that of the Brashear process. The difference can be detected at a single reflection. It is easily detected after three or four reflections. The process has the advantage that the silver is deposited at a normal temperature, which does not require very careful regulation.

(4) THE TARTARIC ACID PROCESS.

So far as brilliancy is concerned, the surfaces produced by this process are nearly comparable with those of the Rochelle salt process. From the point of view of the optician, the process has the disadvantage that the best results can be obtained only when the bath is heated to about 40°C. To subject finished optical parts to this temperature is undesirable. This objection is not applicable to such work as large flat mirrors, in which case steam-heated tables are used. A single deposit only is necessary.

(5) BRASHEAR PROCESS.

This process is probably the one that is most extensively used for the silvering of optical parts. It is a cold process, which gives good results at a temperature between 10°C. and 20°C. It is not unusually complicated, and the resulting coating is brilliant, comparatively hard, and adheres well to the surface of the glass. Coats of any thickness can be obtained by successive deposition. The layer can also be burnished for surface reflection.

Details of all the above-mentioned processes are well known. They may be obtained from any of the books of recipes, such as Spon's. But there is one detail that cannot be too strongly emphasised, namely, thorough cleanliness, which, if neglected, will result in failure, however perfect the appliances and the methods may be.

IMPERFECTIONS.

When the reflector is not near the focal plane small imperfections result only in a loss of light at the emergent pupil, and, although such a reflector may be slightly tarnished or spotted, the optical instrument may still be capable of performing its designed function.

When the silvered surface is in or near the focal plane, minute imperfections that ordinarily would be quite imperceptible may provide sufficient cause for the rejection of the instrument, especially when the power of the eye-piece is high.

Brown stains are usually attributable to impurity of the chemicals and want of cleanliness in conducting the operations and particularly the cleaning of the surface.

Pinholes in the silver which may be due to the evolution of gas bells or to the presence of dust, give rise in the course of time to systems of concentric rings which gradually broaden out. These tarnish rings have but little reflecting power, and are consequently very visible.

An unprotected silver layer on the surface of glass has very little durability. It rapidly tarnishes over the whole surface, and also is extremely liable to become spotted. It is essential that there should be as little time as possible between the silvering and protecting processes. The trouble may be due to atmospheric moisture containing acids associated with particles of dust in the air, which deposit themselves upon the silver surface. But the principal cause appears to be minute particles of saliva. From tests that have been carried out, it would appear that this substance reacts upon silver more quickly than dilute acids and alkalies. Perspiration also acts extremely rapidly on the silver, but a skilled operator exercises care in handling the silver surfaces, and is unlikely to suffer from such a source of trouble. If much time elapses between the silvering and the protecting processes, it is very difficult to prevent minute particles of saliva from landing on the surface. In one instance the number of rejections was greatly reduced by cutting out intermediate operations

between the silvering and protecting operations, and thus reducing the time of exposure and the amount of handling. It will be understood that this applies to minute imperfections which under ordinary circumstances would be regarded as negligible.

Pinholes, when well defined, can be readily detected, but there is an intermediate type in which there is a local sponginess or possibly thinness of the layer. Pinholes or sponginess of this type cannot readily be protected by the electro-deposition of copper, as the pinhole in the silver will be reproduced in the copper as a spongy or thin area. It is not sufficient, therefore, to protect the surface by means of deposited copper without an additional protection of shellac or other varnish, because the coppered surface, if left exposed to the atmosphere, will probably become affected at this point of weakness.

CLEANSING OF THE GLASS SURFACE.

A system that has been found satisfactory in practice when using the Brashear process is as follows :—

The surface is first cleansed with naphtha, then with nitric acid. It is fortunate that the majority of the glasses in ordinary use are unaffected by strong nitric acid. The naphtha, like most solvents, leaves a fine residual film of oil on the surface, which is not removed by the nitric acid. The surface is, therefore, again cleansed with ammonia, followed by nitric acid, and finally by distilled water. It will be understood that the cleansing process should be carried out immediately before immersing the parts in the silvering bath.

When working the Rochelle salt process, after cleansing in the manner described above, the surface is immersed in a bath of stannous chloride, and then well washed in distilled water before insertion in the silvering bath. If there is delay between the stannous chloride treatment and the silvering process, the resultant coat will be unduly brown. The stannous chloride treatment appears to affect the brilliancy of the Brashear coat more than that of the Rochelle salt coat, and it is for this reason that it is not used in the Brashear process. Even in the Rochelle salt process the stannous chloride appears to have an effect upon the brilliancy of the coating. But it has the distinct advantage of producing a more adherent layer.

The action of the stannous chloride is somewhat obscure, and it would be interesting to have the opinions of the members of the Societies. I would suggest that the function of the stannous chloride is to provide a greater concentration of reducing agent directly on the surface of the glass where the deposit is desired than is obtainable from the ordinary liquids of the bath alone. It might be thought that the washing with distilled water would remove all the stannous chloride, but there is reason to believe that is not the case. After washing there appears to be an extremely thin surface film of stannous chloride, which can only be removed with some difficulty with nitric acid, but which is readily removed with hydrochloric acid.

SURFACE SILVERING.

There are many cases in which surface silvering, either on glass or metals, would prove of great advantage, but at the present time it is hardly possible to make such surfaces sufficiently durable. It is well known that thin layers of varnish can be applied to such surfaces, the thickness of the layer when thin being so uniform as not to affect the definition under the highest magnifying powers that are customary. For example, if a drop of varnish composed of celluloid dissolved in amyl acetate

and acetone is dropped centrally upon the reflector mounted upon a quickly rotating table, the varnish under centrifugal action will spread itself in a layer that is sufficiently uniform, provided it is very thin. A varnished surface of this type may appear uniformly coloured when viewed obliquely.

Experiments which the writer carried out some time ago seemed to indicate that, although the layer could be thickened without at first affecting the definition, it tended to become granular or uneven, which is intelligible in view of the enormous contraction of varnishes of this type. Surface-silvered reflectors covered with various varnishes were exposed to the atmosphere, but not directly to the weather. As the atmosphere was that of Glasgow, the test was drastic. After three months the specimens showed signs of tarnishing and spotting. It was observed, however, that in the majority of cases the bulk of the tarnishing was near the periphery, from which it appeared to spread. In a new series which was prepared, the edges were sealed with a thick layer of gum damar varnish. After three months these specimens showed no signs of tarnishing; after six months there was slight spotting; when examined after nine months' interval there appeared to be a progressive increase in the tarnishing and the spots had grown, but it was estimated that the total amount of tarnishing would not have reduced the illumination by more than about 10 per cent. Some time later the specimens were stolen by someone who estimated the material value more highly than the scientific.

The results of the experiments seem to show that, even when the edges are sealed, surface silvering cannot be protected sufficiently well for practical commercial use.

REFLECTIVE POWER.

I had hoped to be able to give the results of a series of tests, but experiments which are in hand for the purpose of testing the absolute and relative reflecting powers of various surfaces are unfortunately not yet complete, and I can only give a few general results.

The test specimens are in the form of slips of glass about 100 mm. long and 3 mm. thick. The ends of the slip are worked to an angle of 45 deg., and the arrangement is such that the entering and exit beams are at 45 deg. to the plane of the slips. Under these circumstances the light is multiply reflected before reaching the eye, the number of reflections being the length divided by the thickness. A small imperceptible loss at a single surface becomes quite apparent after multiple reflection in this way. The amount of the loss is measured by means of a special photometer.

A mercury tin amalgam surface is generally considered to reflect at a single surface about 70 per cent. of the incident light. In this respect the mercury surface appears to be slightly better than a speculum metal surface.

Specimens silvered by the Brashear process were compared with a specimen which was photometrically tested by the German Reichsanstalt, and was certified to reflect at a single surface 98 per cent. of the incident light. The Brashear specimen was slightly superior to this German standard, and, if the German figure is accepted, it may be assumed that the Brashear surface reflects 98 per cent.

One half of a slip was silvered by the Brashear process, and the other half by the Rochelle salt process. There appears to be a difference of 6 per cent.—i.e., the Rochelle salt surface reflects about 92 per cent. Another slip was similarly silvered, one half by the Brashear and the other by the tartaric acid process. The difference was 8 per cent.—i.e., assuming the above value for the Brashear reflection, the tartaric acid surface reflects about 90 per cent. of the incident light.

5.—“THE SILVERING OF GLASS REFLECTORS BY CHEMICAL DEPOSITION.”

By F. ELLERMAN and H. D. BABCOCK.

(Mount Wilson Observatory.)

In the operation of the various telescopes of the Mount Wilson Observatory it becomes necessary to re-silver the mirrors one or twice a year, in order to keep the reflecting surfaces up to maximum efficiency.

We have used several processes for depositing the silver on the glass, and have come to prefer the so-called “Brashear Process.” This process gives thick, brilliant and hard coats, which will withstand a great amount of burnishing—an operation which the mirrors used for solar work need once or twice a week.

In our experience in silvering we have found it profitable to double coat, that is, to divide the quantity into two parts, and deposit one coat on top of the other. By this method one obtains coats 40 per cent. to 50 per cent. thicker than when using the entire batch of chemicals on one solution.

The temperature of the solutions and mirror should be 60° or 65°F. If the temperature is too high the deposit will be too thin and delicate, if too cold it will be thin or granular.

Stock-reducing solution is made up as follows:—

Distilled water	100 oz. fluid
Pure grain alcohol	12	“ “
Rock Candy (from cane sugar)					10	“ troy
C.P. Nitric Acid...	½ “ fluid

This is allowed to age for at least one month before using. This keeps indefinitely, but increases in vigour and rapidity of action when age reaches several years.

The quantities we use are very easy to remember. To coat a glass, we take, for each square inch of surface, 2 grains of silver nitrate, two-thirds as much caustic potash or caustic soda, and 10 times as much reducing solution as caustic. In silvering our 60-in. mirror (an area about 2,830 sq. in.) we use:—

Silver nitrate	12 oz. troy
Caustic potash or soda pure by alcohol					8	“ “
Reducing solution	80	“ fluid

Modus Operandi.—This quantity is divided into two portions, each of 1 oz. silver nitrate dissolved in 16 oz. water. This is the reserve silver to be referred to below. The other 5 oz. nitrate are dissolved in a 3 gallon jar containing 1 gallon distilled water. The 4 oz. caustic are dissolved in 1 quart of water, and cooled before using, as fulminate is apt to form readily if used while warm.

To the 5 oz. silver nitrate solution C.P. ammonia is added until the brown precipitate first formed is re-dissolved, the solution being stirred constantly. The caustic solution is now added slowly, while stirring vigorously. The precipitate which is formed is black for caustic potash, and somewhat brownish for caustic soda. When the caustic is all added, ammonia is again added, slowly, and when there are indications of clearing, caution should be exercised not to add more ammonia than just enough to clear the liquid. The reserve silver is now added slowly

while stirring, and when the precipitate which forms is no longer completely redissolved, the liquid becomes yellowish. When this stage is reached the addition of silver must be made with caution so as not to go too far. The colour should be slightly brownish or deep straw colour. If the reserve silver is not all used up when this stage is reached a few drops of ammonia are added and then silver, alternating until all of the reserve silver is used up, and the liquid is of a deep straw colour. It is better to have it a little dark than too light. Filter through absorbent cotton to remove floating particles.

The mirror, properly cleaned, and made into a dish by applying a band with a spout, made of metal, lined with muslin and thoroughly coated with paraffin wax, is now ready for the solution. Enough distilled water is poured on the glass to cover it about $\frac{3}{4}$ in. deep. The silvering solution is divided into two equal quantities, preferably in pails for handling, and 20 oz. reducing solution added to each, and immediately poured on the mirror, rocking the mirror in order that the solution and water mix thoroughly. When the liquid has reached the muddy stage and the flocculent particles begin to settle on the silver coat, the surface is gone over, gently at first, with swabs made of absorbent cotton, to brush these particles loose. The swabbing is kept up until the liquid begins to clear, then it is poured off and rinsed with distilled water, then left standing and enough water poured on to cover the mirror as before silvering. The second half of the materials are now prepared and the silvering operation is repeated.

When the second coat is done, and the liquid poured off, the subsequent rinsing and washing is done with tap water or ordinary water free from chlorides or other impurities. The silver surface is scrubbed with cotton swabs for 10 to 12 minutes. This scrubbing removes some of the bloom which may have formed, and cleans the surface free of the chemicals.

It sometimes happens when silvering 15 in. to 30 in. mirrors, that when the last washing water is poured off, the water will leave the silver coat quite dry, except a few strings of drops adhering to the surface. These are absorbed with white blotting paper. In the case of the large mirrors, after pouring off the water, the surface is wiped as free from water as possible with wads of damp cotton, then alcohol is poured on the middle and spread over the surface with cotton. This drives out the water and dries the surface free from streaks.

The surface is now burnished for half an hour with a cotton pad, then a clean chamois leather pad is used. This burnishing knits the silver and makes the surface harder. If the bloom is not entirely removed, a little powdered rouge is added to the pad. After polishing is complete, we again go over the surface with chamois pad free from rouge, which burnishes out the minute scratches from the rouge and makes the surface more resistant to the action of the air impurities.

When the bloom is difficult to remove, we do not attempt to get it all out at the time of silvering, but let it work off during the subsequent burnishings. In such cases the surface is apt to be more brilliant after several weeks' use than when new.

6.—“THE SILVERING OF A LARGE REFLECTOR.”

By C. R. DAVIDSON.

(Royal Observatory, Greenwich.)

The method employed at Greenwich is essentially the Brashears process, with slight modifications, a description of which was published by Mr. Brashears in the “English Mechanic” in 1893. Its merit is that it gives a hard enduring film which will stand a considerable amount of polishing.

The formula as used is as follows :—

- A. 10 per cent. silver nitrate solution.
- B. 25 per cent. ammonia (0.880).
- C. 10 per cent. caustic potash solution.
- D. Reducing solution :

Distilled water	2,000 c.c.
Sugar	180 grms.
Nitric acid	8 c.c.
Alcohol	350 c.c.

A, B and C may be made as required. The reducing solution should be made up several months before it is required, as when freshly made it is not very active. It may be improved by boiling, the alcohol being added after it has cooled.

The silvering bath is made up in the following proportions :—

A. (silver nitrate)	20 c.c.
B. (ammonia)	10 c.c. (more or less)
C. (caustic potash)	10 c.c.
D. (sugar)	5 c.c.
Distilled water	100 c.c.

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To prepare the bath :—

Of A (silver) take, say, 100 c.c. and to this add B (ammonia) gradually. The solution at once turns brown. Continue adding ammonia, in quite small quantities, until the solution clears or nearly clears. Now of C (potash) add 50 c.c. The mixture will again thicken, turning dark brown. Again slowly add ammonia as before, keeping the solution agitated till it again clears. The solution will now be a pale brown colour but transparent. This part of the operation is a critical one, as it is important to avoid an excess of ammonia. In fact, it is absolutely necessary to have a slight excess of silver in the solution, and this is secured by now adding silver drop by drop until the solution will take up no more, and a little brown matter is left in suspension.

To 500 c.c. of distilled water add 25 c.c. of D (sugar).

When the silver-potash solution is added to this the bath is completed, but this must not be done until the mirror is ready for silvering.

A mirror may be silvered either face upward or down as circumstances decide. Small work is preferably silvered face down, but large mirrors are more easily handled face up. The dish for the bath should be of glass or porcelain, but large baths may be of wood or sheet metal thickly coated with paraffin wax, and for economy should

be of nearly the same size as the mirror to be silvered. In the case of very large mirrors it is most economical and convenient to make the mirror itself form the bottom of the bath.

The following is the procedure when silvering the Greenwich 30 in. reflector : The walls are made by wrapping a band of paraffined cartridge paper about 5 in. wide two or three times round the mirror, leaving about 3 in. above the surface, and sealing it to the glass with paraffin wax. The making of the joint between the paper wall and the edge of the mirror is important, as any small crevices which are left serve as pockets to retain the nitric acid with which the mirror is cleaned. This is avoided by not winding the paper straight on to the mirror, but first introducing a paper packing ring about $\frac{1}{4}$ in. thick, the top of which comes $\frac{1}{4}$ in. below the edge of the glass. The paper band is wound on over this and a channel $\frac{1}{4}$ in. in depth is left between the paper wall and the mirror which is filled by running in hot paraffin wax. This makes a smooth clean joint from glass to paper and has proved perfectly satisfactory.

The dish is now ready. The mirror is supported by an iron ring with three lugs, and with cords and tackle is suspended at a convenient height so that a conical rotary motion may be given to it when the silvering solution is poured on.

Cleaning.—The cleaning is one of the most important operations. Unless the work is absolutely clean failure must result. All dust is removed and the old silver cleaned off with strong nitric acid, using a swab of cotton wool. Considerable pressure should be applied and the swabbing should be very thorough. Wash with water and with nitric acid swab again. Rinse off the nitric acid using plenty of ordinary water followed by distilled water. Finally, leave the mirror standing completely covered with distilled water. It is now ready for silvering. In the cleaning operation it has been recommended that the nitric acid be followed with a swabbing with caustic potash. Our experience is against this, the nitric acid being more easily removed than the potash.

We now proceed to prepare the bath :—

For the 30 in. mirror 8,000 c.c. of solution is required. This is sufficient to give a minimum depth of about 1 cm.

Of A. (silver) take	1,200 c.c.
B. (ammonia)	600 c.c.
C. (potash)	600 c.c.
made up as described above ;					
and Distilled water	6,000 c.c.
D. (sugar)	300 c.c. (or as experiment shows).

In addition to the varying activity of the sugar solution the temperature has a very large influence on the result. Working under somewhat unfavourable conditions, it is not practicable to exercise much control over this factor.

A temperature of 65° - 70° is recommended as giving the best results, but with the 30 in. we have generally to be content with a temperature not much above 55° , and the proportion of reducing solution has to be increased to suit that condition. It may be taken, however, that if the temperature is too high, reduction will be too rapid, and the resulting film soft, whilst if too low action is very slow and the film too thin.

The amount of sugar solution required must be found by experiment at the time of silvering by making three small test baths, using :—

- (1) normal reducer
- (2) 25 per cent. more
- (3) 25 per cent. less

and judging by the result.

We left the mirror covered with water. This is now thrown off and the water and sugar poured on ; then the prepared silver potash solution is added. At the same time a conical swing is given to the suspended mirror so that a continuous wave passes round the bath. This must not cease until the exhausted solution is thrown off. The drawback to the Brashear process is the formation of sediment which must be prevented from settling on the mirror surface by keeping the solution constantly in motion. This may be further assisted in the following manner :—

Immediately the prepared silver is added to the water and sugar it begins to darken and in two or three minutes there will be a visible coating of silver. As soon as there is an appreciable deposit it will be found tough enough to stand light swabbing with cotton wool. Using rubber gloves the operator takes a handful of cotton wool and draws it lightly over the surface, exerting no pressure beyond the weight of the swab itself. This will disturb the heavy sediment which, as the bath gets thicker, the motion of the solution is unable to prevent falling. As the cotton becomes dirty it is thrown away and a fresh handful taken.

It is a difficult point to decide when to throw off the solution. If too soon, the film will be bright but thin. If too late, the deposit will be thicker but clouded and will require much polishing. The former alternative is preferable. One must be guided by the preliminary experiments and experience.

When the silvering is judged completed, throw off the spent solution as quickly as possible, tear off the paper wall and wash thoroughly with distilled water. If lightly swabbed during the washing much of the cloudy bloom on the surface will be removed, and when dry it will be found to require very little polishing. Stand the mirror in a tilted position to dry and in an hour it will be ready for polishing.

The polishers are made of best chamois leather stretched and tied over a ball of cotton wool. Two are necessary. First with a plain rubber go over the entire surface with light circular strokes, dusting constantly. Then rub a little rouge into the other and repeat. If the film is a good one it will take a high polish with very little rubbing and with very little scratching. The rubber must be scraped from time to time or any particles that may be polished off will cause scratching.

7.—“NOTE ON THE SILVERING OF GLASS AND QUARTZ FIBRES.”

By ROBERT S. WHIPPLE, M.I.E.E.

(The Cambridge and Paul Instrument Co., Ltd.)

Although the silvering of glass or quartz fibres is not intended for the production of reflecting surfaces, yet the technique of doing so may be of interest.

In the Einthoven string galvanometer a silvered glass or quartz fibre is stretched in a strong magnetic field, the silvered fibre acting as a conductor and forming the moving system of the instrument.* It is important that a hard and homogeneous film of silver should be deposited, as the resistance of the fibre should remain as far as possible constant; and that connecting wires should be soldered to the silver. In practice it has been found that a more homogeneous film of silver can be deposited on a glass than on a quartz fibre, and for this reason the glass fibre is frequently used in preference to the quartz one. The fibres, which are about 7.5 cm. long and from 0.0015 to 0.003 mm. in diameter, are produced by the method described by Souttar.† In this method the fibres are drawn by means of a falling weight from a glass rod or tube of small diameter heated in a small electric furnace. A group of fibres made in this way is shown ready for silvering in Fig. 1.

Before the fibre is drawn the rod or tube from which it is to be made should be free from grease by rinsing in benzol. In the case of tubing care should be taken to see that the bore is clean as well as the exterior surface. After drawing no other cleaning is necessary, but the fibres should be silvered on the same day they are drawn and in the interval between drawing and silvering should be protected from floating dust particles by being placed in an air-tight box.

Quartz fibres are generally made by means of a bow and arrow after the Boys' method;‡ if possible they should be silvered on the same day as they are drawn. If this is not possible, and the fibres have been made some time, then it is imperative that they should be cleaned. The fibres should first be dipped into concentrated nitric acid and then into a strong solution of caustic potash. After the latter bath they should be washed in distilled water and absolute alcohol. The Rochelle salt process of silvering, the details of which are well known, is employed. The actual solutions used are

A.—Silver nitrate, 10 grammes.

Distilled water, 1,000 c.c.

B.—Silver nitrate, 2 grammes.

Rochelle salts (sodium and potassium tartrate), 1.66 grammes.

Distilled water, 1,000 c.c.

In making up the solution the distilled water should be brought to the boil, and first the silver and then the Rochelle salts should be added, both of which have been dissolved in the smallest possible quantity of boiling water. The boiling is then

* “Ein neues Galvanometer,” by W. Einthoven, *Annalen der Physik*, Vol. XII. (1903), p. 1059 (and subsequent volumes). See also “The Mechanism of the Heart Beat,” by Dr. Thomas Lewis. - Publ. by Messrs. Shaw & Sons, London.

† “Demonstration of a Method of Making Capillary Filaments,” by H. S. Souttar. *Proc. Phys. Soc., Lond.* Vol. 24, p. 166 (1912).

‡ “On the Production, Properties and some suggested uses of the Finest Threads,” by C. V. Boys, *Phil. Mag.*, June (1887), p. 489. See also “On Laboratory Arts,” by Richard Threlfall, p. 196. Publ. by Macmillan & Co., London.

continued for about twenty-five minutes until the grey precipitate has collected in the form of a compact powder at the bottom of the flask, leaving the liquid nearly clear. It should then be filtered whilst hot, the liquid being perfectly clear and remaining so when cold; it may be found necessary to filter two or three times.

A great deal seems to depend upon the length of time of the boiling as regards the performance of the silvering bath. The longer the boiling the more rapidly will

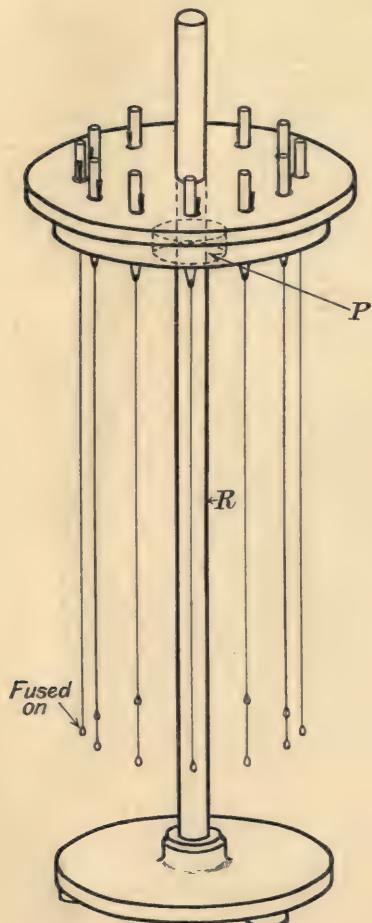


FIG. 1.

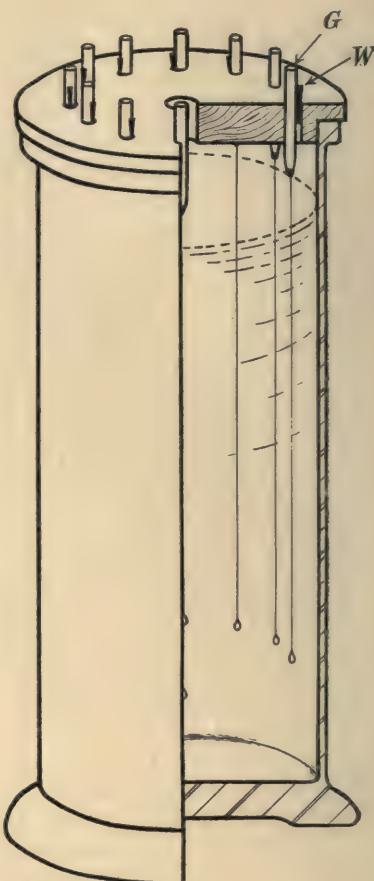


FIG. 2.

the deposit take place and the more uniform it will be.* Perfectly prepared solutions will keep for about a month.

The simplest way to handle the glass fibres for silvering is to arrange them round a wooden disc as shown in Fig. 1. The disc rests on a projection *P* on the supporting rod *R* and whilst in this position the fibres are placed in position. The fibre with its

* See "Notes on Silvering Solutions and Silvering," by F. L. O. Wadsworth, *Astrophysical Journal*, Vol. I., p. 252 (1895).

little weight (made during the manufacture of the fibre) is threaded through one of the holes in the disc and is held in position by means of a wedge *W* (Fig. 2), which pushes the thicker glass rod *G* (from which the fibre was drawn) against the sides of the hole. Twelve fibres can be carried by the disc without difficulty.

Equal volumes of the two solutions *A* and *B* and of distilled water are quickly mixed and poured into a glass jar. The disc carrying the fibres is then carefully lifted off the supporting stand, and the fibres lowered into the solution until the disc rests on the top of the jar as shown in Fig. 2. As the metallic silver commences to deposit immediately the two solutions are mixed, no time should be lost between mixing and the immersion of the fibres. After immersion for two hours the fibres should be taken out and hung in a dust-free position to dry for about 12 hours. After this time they should be ready for mounting.

In the case of quartz fibres the same procedure can be employed except that the fibres will require shellacing (by means of fused shellac) to small cylindrical pieces of glass on wire, so that they may be clamped into the holes in the wooden disc. Small pieces of shellac should also be stuck on the end of the fibres to act as weights. It will be found that the shellac resists satisfactorily the action of the solution. If it is desired to silver a few fibres separate ones may be silvered in large test tubes. In this case a cork with a wire inserted through it will be found a satisfactory support from which to suspend the fibre.

To obtain satisfactory results it is essential that the chemicals used should be chemically pure and that the distilled water should also be pure. If there is any doubt as to the purity of the water it should be re-distilled. It is important that all the vessels used should be cleaned with nitric acid and finally rinsed with distilled water. After use any silver deposited on the walls of the vessel may be readily removed by nitric acid.

The film of silver deposited is surprisingly hard, and if care is taken it may be soldered to fairly heavy brass wires or other supports. These should be reduced in thickness at the point where the fibre is attached. A solder made of the following constituents will be found efficient if care is taken not to overheat the soldering iron :

Bismuth	50	parts.
Tin	31.25	"
Lead	18.75	"

The silver coating may be polished by means of a copper wire lightly rubbed along the surface.

The approximate resistance of a silvered fibre 7.5 cm. long and 0.003 mm. in diameter is 2,500 ohms. The resistance can be increased by reducing the length of time the fibres are in the silvering solution.

8.—“SOME NOTES ON MIRRORS USED FOR REFLECTING HEAT RADIATION.”

By PROF. CHAS. FÉRY.

(École Municipale de Physique et de Chimie, Paris.)

Some metals, such as gold and silver, take a fine polish and reflect 98 to 99 per cent. of the heat radiation falling upon them. For this reason they have been largely used in a certain number of instruments, particularly in radiation pyrometers, the action of which is based on Stefan's law. Silver, unfortunately, dulls quickly in air, and the same effect occurs—although in a lesser degree—with the old bronze alloy (speculum metal) from which the mirrors of astronomical telescopes were made.

An endeavour was made to electro-plate bronze mirrors with a thin coating of gold, but this process, which should have given good results, was abandoned. It was found very difficult to obtain a thin coating of gold without any break in the continuity of the surface. If only one spot of the metal was not covered by gold, this spot became an electric cell, and under the influence of humidity and fumes which are found in works where pyrometers are used, the bronze was attacked sooner than if it were not covered with gold. It was found that a spot was formed which became larger and larger, and thus gradually reduced the amount of radiation reflected by the mirror. I then thought of using silver again, which deposits easily on glass mirrors and these are lighter and easier to polish and to make than metal mirrors. To avoid the oxidation and sulphuration of the metal, it is sufficient to cover the silvered surface with a varnish which does not absorb the heat radiations. It is known that all bodies which contain oxygen have low diathermancy, and that on the other hand the hydrocarbons are very transparent. Judee's bitumen, which is a natural hydrocarbon, can be made into an excellent varnish which possesses the advantage of hardening under the influence of light. This property has caused it to be used in photogravure, for, as is well known in this process, it resists the action of nitric acid used for etching the zinc. The experiment has proved that this varnish prepared with a suitable absorbent (benzine is too volatile) gives a very regular and thin coat which absorbs only 3 per cent. of the total radiation reflected by the silver. The colour of the mirrors which are thus treated is almost identical with that of gold, and the mirrors do not show any selective absorption in the infra-red. The varnish appears to be extremely hard, and the mirrors may even be dipped into ammonium sulphide without suffering. They can be cleansed by washing, without difficulty. Their price is less than that of any other mirrors that are intended for the same purpose.

Editorial Note.—Judee Bitumen varnish may be obtained from M. Detourbe, 7, Rue St. Séverin, Paris (London House, 79, Coleman Street, E.C.), under the name of “Vernis à recouvrir.” It appears to be a solution of bitumen in French turpentine.

French turpentine does not seem to be readily obtainable in this country, but either American spirits of turpentine or commercial pseudo-cumene (or pseudo-cumol) may be employed as solvents for bitumen. Powdered Judee Bitumen may be obtained from Billault Chenal, Douilbret & Cie Succrs., 22, Rue de la Sorbonne, Paris. Pseudo-cumene may be obtained from Messrs. Harrington Bros., Oliver's Yard, City Road, London.

The varnish made with pseudo-cumene is a little more transparent and of a slightly better surface. It has also the possible advantage that the pseudo-cumene is entirely volatile. With turpentine there is always the chance of some change during oxidation of the solvent.

9.—“DEPOSITION OF METALS BY CATHODIC SPUTTERING
IN VACUO.”

By F. ELLERMAN and H. D. BABCOCK.

(Mount Wilson Observatory.)

Opaque or partially transparent mirrors of silver, gold, platinum, nickel, copper, and occasionally other metals, are frequently prepared in our laboratory, mainly for use in interferometry. In our experience the best conditions for successful deposition are not identical for the various metals, but are in general much the same. Silver is most commonly used for the visible part of the spectrum, copper for the infra-red, platinum and nickel for the ultra-violet.

Our sputtering chamber consists of a glass bell jar 8 ins. high and 4 ins. inside diameter. Its base is ground to fit a sheet of plate glass mounted upon a wooden support, and its vertex is pierced by a ground-in glass tube which carries an aluminium electrode. Through the glass base plate pass a pump connection and another glass tube through which is sealed a wire for electrical connection to the cathode. The cathode is a sheet of the metal which is to be sputtered, about 2 ins. square. It is supported horizontally upon a short piece of large glass tubing so as to be about an inch above the base plate. A light tripod stand made of glass rods supports the plate which is to receive the metallic coating, face downward, at a height of $1\frac{1}{2}$ ins. above the cathode. The parts are cleaned and assembled, using a small quantity of grease on the edge of the bell jar. After seating the bell jar in place, a small quantity of stop-cock grease is run around the outside of its base, using a small pointed gas flame to liquify the grease. A mercury pump is used to remove the air until the pressure is such that the dark space next the cathode reaches just up to the face of the mirror. No attempt is made to remove the traces of mercury vapour and of hydrocarbons which are invariably present with this procedure.

The discharge current is supplied by a 300-watt transformer having a ratio of 10,000 to 100 between its secondary and primary voltages. The low tension side is connected to the lighting system with a ballast resistance in series. The high tension side is connected to the bell jar terminals, through a small mechanical rectifier operated on the shaft of a tiny synchronous motor of very simple type. The ballast resistance is regulated so as to deliver a current of about 0.02 ampere through the bell jar. If the pressure becomes too low, or the discharge current too great, the metallic mirror becomes covered with minute pits, which diffuse much of the light instead of regularly reflecting it. Under the conditions stated above, a silver or gold film of medium thickness is ordinarily deposited in about ten minutes. It sometimes happens that, during the first few minutes of operating the sputtering chamber, a brown film is deposited, after which the metal comes clean. A cathode generally works best after it has been in use for some time. The purest obtainable sheet metals are used for electrodes.

The above method, whilst very satisfactory for small mirrors—not exceeding 3 ins. diameter—has not proved so successful for large mirrors.

10.—“NOTE ON THE PRODUCTION OF MIRRORS BY CATHODIC BOMBARDMENT.”

By F. SIMEON, B.Sc., F.Inst.P.

(Messrs. Adam Hilger, Ltd.)

The production of mirrors by cathodic bombardment is not a new process. Workers with vacuum tubes since Grove, 1852, have noticed the bright deposit in the neighbourhood of platinum electrodes, which is more or less marked according to the current passed through the tube and nature of the residual gas. This deposit is generally objectionable, and was especially so in the case of the older form of X-ray bulb with platinum anti-cathode. This disintegration is not peculiar to platinum, nor indeed is platinum the most easily deposited metal. Sir William Crookes in 1891 investigated the relative rates of sputtering of a number of different metals under similar conditions of discharge. The relative rates are given in the following table, in which the rate for gold is taken as 100* :—

Palladium	...	108.80	Platinum	...	44.0	Iridium	...	10.49
Gold	...	100.00	Copper	...	40.24	Iron	...	5.50
Silver	...	82.68	Cadmium	...	31.99	Aluminium	...	0.0
Lead	...	75.04	Nickel	...	10.99	Magnesium	...	0.0
Tin	...	56.96						

Many other observers both before and since have investigated various points having some bearing upon this method. A bibliography of their papers will be found in the reference given.

A convenient apparatus consists of a vacuum tube of special form which permits of readily altering the cathode and of introducing and removing the various objects (glass plates, &c.) which it is desired to coat with a reflecting surface. The vessel employed in the apparatus exhibited is a vacuum dessicator, through the upper part of which is introduced, in addition to the exhaust tube for connection to the vacuum pump, two aluminium wires covered with glass tubing for insulation. To one of these, which is introduced centrally, can be attached a disc of the fine metal of which it is desired to form a mirror. The other, after emerging from the glass tube, is bent into a portion of a circle, in about the same horizontal plane as the surface to be coated, and so as to be as far removed from the surface as the vessel allows. These wires are connected externally to an induction coil, a Lodge valve also being included in the circuit. The article to be coated, after being scrupulously cleaned and dried, is placed upon a clean glass support in the lower part of the vessel. Connection between the two parts of the vessel is made with some form of vacuum grease, great care being exercised that neither the surface to be coated nor the cathode itself is in any way contaminated, as this will lead to some blemish in the final result. The vessel is exhausted until the cathode dark space extends nearly to the work.

The mechanism of the process is undoubtedly that particles of the metal are projected from the cathode by electric repulsion of like charges. Two observations may be made about the results. First, the metallic films in general adhere more firmly than by other methods of deposition, and secondly, the thickness of films is built up gradually, so that semi-transparent films are formed before perfectly opaque ones, and thus the time required to produce a surface depends upon what degree of transparency is

* V. Kohlschütter, Jahrb. d. Radioaktivität, Vol. 9, pp. 355-418 (1912).

required. There are other factors which affect the time of deposition beside the nature of the metal itself. It decreases with the rise of current through the tube and with the cathode fall of potential. The nature of the gas in the vessel is another factor influencing the time, which is in general shortened by the use of the heavier gases. A further important factor is the temperature of the cathode, the sputtering being in general increased with rise of temperature of the cathode. In fact, a method has been described in which silvered surfaces are produced by passing an incandescent silver wire across the object in *vacuo*.* This, however, is purely a temperature emission, as no high tension current is required.

It will be noticed from the table given above that the order of metals is roughly that of decreasing atomic weight. Perhaps the most outstanding departure from the generalisation is that of silver, which appears near the head of the list. An examination of the reflecting powers of various metals for different wave lengths of the spectrum (see Wood's "Optics," 1911, p. 466) shows that while silver is the best reflector for the visible part of the spectrum, it fails badly in the ultra-violet; in this region nickel is perhaps the best reflector of any pure metal. These figures are the results of Hagen and Rubens' work in 1902. More recent work by Hulbert† has confirmed this, and extended the knowledge of the reflecting powers of metals in this region, and he has shown that silicon has exceptionally high reflecting power. For the infra-red, gold is as good as silver, and is to be preferred on account of its greater stability in ordinary atmospheric conditions.

Examples were shown of these metals, and also of palladium and platinum deposits which yield bright and durable mirrors for use in galvanometers, &c.

* Stuhlmann, *Journal Am. Opt. Soc.*, Vol. 1, No. 2, pp. 78-83 (1917).

† Hulbert, *Astrophysical Journal*, XLII., pp. 205-230, October (1915).

11.—“ PLATINUM REFLECTING SURFACES PREPARED BY THE ‘ BURNING-IN ’ PROCESS.”

By JULIUS RHEINBERG, F.R.M.S., F.R.P.S.

INTRODUCTORY.

If certain mixtures containing platinum salts are spread on a glass surface, and the glass submitted to a suitably high temperature in a furnace, a mirror-like reflecting surface of a permanent nature is produced. This is the so-called “burning-in” process, and it has been known for a long time; indeed, I have been told that such glasses were exhibited at the first International Exhibition at the Crystal Palace.

Apparently the exact methods used and the precise composition of the mixtures used have been kept secret by those who have practised them, and they are still being practised in France, and I believe elsewhere, and all that I have been able to ascertain from reference to literature is, that the platinum salts are mixed with various viscous and oily fluids, such as oil of lavender, &c.

Now if such a mixture spread on glass is evaporated in a furnace, it is evident there will be bubbling and ebullition, and great disturbance during the process, particularly so when there are several fluids evaporating at different rates, and the resulting mirror formed will not be structureless and homogeneous, but will show a more or less pronounced grain. A granular surface of this description would not reflect light in a *perfectly* regular manner, but would to some extent reflect it irregularly, or in other words scatter or diffuse the light; and in addition, if any untoward chemical compounds are produced which combine with the glass, or enter the ultra-microscopic pores of the glass, along with the ultra-microscopic colloidal particles of pure platinum, then we would obtain increased irregular diffusion of light from the glass surface. And that is what appears to have actually been the case with mirrors produced by the “burning-in” process hitherto; this constitutes one of the reasons, probably, why for optical purposes there has been little use for such mirrors.

A few specimens of a “burnt-in” semi-platinised mirror, of a French make, which I understand to have been about the best available, are exhibited this evening, to illustrate the above observations.

PROCESS EMPLOYED.

It is apparent from the foregoing that, in order to obtain a structureless, homogeneous mirror, which would reflect light perfectly with a minimum of diffusion, the coating mixture for the glass, containing the platinum salts, should be one which is perfectly combustible and should at the same time burn off or be evaporated regularly and evenly, without disturbing the platinum contents by ebullition, &c. I hit upon the plan of dissolving the platinum salts in a solution of collodion, which when the glass is coated with it forms a dry film, which has the desired properties.

Now I referred above to the fact that if several fluids which evaporate at different rates are evaporated in a furnace, disturbance and thereby want of homogeneity are caused in the resulting layer, and what is true of violent evaporation under high temperature is also true to a more limited extent at normal temperatures. It is a fact sometimes overlooked that, if a colloid film is formed by evaporation of the material from two solvents, which evaporate at uneven rates, that film is not so regular and even as if it had been formed by evaporation from a single solvent, or

two solvents having a more nearly even rate of evaporation. Collodion is precisely an example of this fact, as it is in nearly every case produced from pyroxiline dissolved in a mixture of ether and ethyl alcohol, because neither of these will dissolve it singly. These two solvents evaporate at very uneven rates, and for that reason it requires an expert to coat glass with collodion properly without noticeable ripples and ridges during the coating, which mean unevenness in the settling of the film, even though such unevenness is subsequently hidden. Therefore I do not make the collodion for this purpose with ether and ethyl alcohol, but dissolve the pyroxiline in the single solvent, methyl alcohol, which I had already found to be a particularly useful solvent for producing collodion films for other purposes, as the solution flows smoothly and regularly, without requiring the special skill necessary with ether-alcohol mixtures. This is equally the case if ethyl alcohol is subsequently added to the methyl alcohol collodion solution, as the difference in the rate of evaporation between methyl and ethyl alcohol is comparatively small.

Suitable glass, on which a collodion film, produced from a methyl alcohol collodion solution, has been formed, will, after subjection to the necessary temperature in a furnace, be found to have the requisite structureless permanent platinised mirror surface, but it was also found that the temperature to which this glass had to be raised was so uncomfortably close to that which would render the glass itself viscous, that the danger of deformation of the glass surface was excessive, despite every precaution.

The next point was therefore to find means of obtaining the result at a lower temperature, and from a study of the literature of ceramics it was decided to try the addition of small amounts of lead salts in the collodion mixture. Various lead salts were tried in varying amounts, and the experiments met with a fair amount of success, the requisite temperature being lowered thereby by 20°C. or 30°C., but the results were not quite satisfactory ; owing to some kind of chemical combination that occurred, the reflecting surface lost in brilliancy and became slightly opalescent (which translated into optics means occurrence of light diffusion), and also acquired a tendency to be spotty in parts. It was then decided to experiment with various salts of bismuth, and after numerous trials this was found to give the desired results, as they were free from the defects appertaining to the use of lead, whilst the lowering of temperature was, if anything, more marked.

Platinum coating mixtures were in this way arrived at, of which the following may be given as a typical example :—

6 per cent. Collodion dissolved in Pure Methyl Alcohol...	3 parts by vol.
Platinum Chloride in the form of 6 per cent. Chloro-	
platinic Acid (H_2PtCl_6) dissolved in Industrial	
Spirits	3 parts by vol.
Industrial Spirits	3 parts by vol.
1 per cent. Bismuth Chloride Solution	1 part by vol.

It should be mentioned that the last-named solution is made up by dissolving 5 per cent. bismuth chloride in industrial spirits with the addition of 5 per cent. hydrochloric acid, and it is diluted with further industrial alcohol just before use, as very weak solutions of bismuth chloride will not keep for any length of time.

In the platinising furnace the glass with a collodion film formed from such a solution passes through successive stages, at successive temperatures. The collodion film first chars and completely volatilises, leaving the reduced platinum in an exceedingly fine state of division in the form of a loose deposit—so loose that it will take

finger impressions, or be removed by writing on with a soft or hard point. Already at this stage it forms a semi-transparent, structureless mirror, and should form an ideal surface for such purposes as recording impressions from harmonographs, oscillographs, and for physical experiments of that description, especially as they can subsequently be made permanent. At a further rise in temperature this loose deposit becomes an adherent deposit, which writing with a hard point will remove, or which hard rubbing will remove. In this stage it is already firmer than a chemically deposited silver or platinum film. In the next stage the platinum deposit is partially incorporated in the surface layer of the glass (partially burnt in), and partially firmly adherent to same. Platinised surfaces that have reached this stage may be cleaned up by wiping, either dry or with spirits, or with spirits and ammonia, or even with a small amount of rouge ; in fact the only means I have found for wholly removing the platinum is by prolonged immersion for days, or weeks, as the case may be, in aqua-regia, frequently made up afresh. Lastly, in the final stage, the platinum is wholly incorporated within the glass surface layer, and is then absolutely permanent. When this stage has been reached, the point of a penknife may be run over the glass without affecting the mirror, *i.e.*, nothing that is not sufficiently hard to damage the glass itself will damage the mirror. Nor will any chemical (except possibly prolonged immersion in aqua-regia) affect it, other than an acid like hydrofluoric acid, which attacks the glass itself. It is, however, necessary to remember that the glass surface layer with the platinum incorporated in it is exceedingly thin, so that if rubbed an excessive number of times, the layer itself may be gradually worn away, as occurred in some experiments with platinised surfaces for dentists' mirrors, which are sterilised and wiped by the dentist very many times a day. Mirrors so treated showed signs of the surface layer being worn through after use for some weeks.

DEPTH OF PENETRATION.

The exact depth to which the platinum has penetrated the surface in a surface mirror is a matter of some interest ; it has not been measured yet, but judging by analogy with the experiments of Beilby, I should be inclined to estimate its thickness as approximately 200 micro-millimetres, or one-third of a wave length of red light.

In consequence of the ultramicroscopic size of the platinum particles and the absence of visible structure, a surface mirror of this description is always transparent, or, more strictly speaking, semi-transparent. The depth of tint of the film can be very nicely regulated and standardised by varying the amount of platinum salts put into the coating mixture, and varying the viscosity of the coating solution (on which the thickness of the collodion film formed will depend) by increasing or decreasing the amount of industrial alcohol. There is, however, a limit to the amount of platinum salts that can be conveniently introduced into a collodion coating mixture to produce a nice, easily flowing solution, and there is also a limit to the thickness which the collodion film should have in order that the glass may platinise nicely, and take up the whole of the platinum. In practice it is not found advantageous to attempt to obtain beyond a certain depth of tint at one platinising, a tint at which the glass will reflect 50 or 60 per cent. of light incident on it, and transmit the remainder. Such glass may be described as semi-platinised, and in order to platinise it fully, the glass after being carefully cleaned with spirits and ammonia is recoated with the coating mixture, and the process gone through again. It is quite possible to repeat the process three or four times, but more than twice is rarely necessary.

QUALITY OF GLASS AND BEST TEMPERATURE FOR PLATINISING.

The facts already mentioned, as to the nature of the platinising and the stages in the process, lead to considerations relating to the best kinds of glass suitable for the process. Many kinds of glass, and also quartz, can be successfully platinised. Those, however, which have been found most suitable are glasses of the type of hard crown, ordinary plate glass and sheet glass, and also micro cover-glass. Glasses containing much lead, *i.e.*, flint glasses, will not yield good results by this process ; the surface of the glass, in fact, loses its transparency. Glasses containing barium appear to be of a denser nature, *i.e.*, have smaller or differently shaped ultramicroscopic pores, which will not admit the sub-microscopic particles of platinum to the same extent as ordinary crown or plate glass.

Temperature control of the glass during platinising, to which I will refer later on, has to be regulated very accurately to within 5° or 10°C. during the process of platinising. It will readily be understood that the composition and the homogeneity of the glass, and the nature of the glass surface play a very important rôle, and that for the purpose of optical mirrors, the platinising temperature will be different for every kind of glass. Unworked plate glass will therefore yield good or indifferent results, so far as permanence or flatness of the resulting surface mirror is concerned, according to whether the surface skin is fairly homogeneous over the piece platinised ; in other words, whether the whole of the surface has been chilled equally in manufacture, or not. Otherwise one part may have attained one stage of platinising ; whilst another part has attained the next stage. Where, however, the retention of the maximum flatness of surface is not of primary importance, for example, for platinised surfaces for electrical purposes, this is of no account, as equally permanent platinising is then obtained by raising the temperature 20 deg. or 30 deg. C.

Similarly, although sheet glass is platinised easily enough, owing to its want of homogeneity such mirrors are useless for optical purposes. In the case of optically worked glasses, whether plate or crown glass, it will be evident from the foregoing that a piece of plate glass must have been ground down sufficiently for the surface for platinising to be of fairly homogeneous structure, and not merely worked superficially so that parts of the hard skin and parts of the softer substance underneath form the surface. And in worked optical glass homogeneity is also of first importance. It will not infrequently happen that in platinising 20 or 30 discs from a single batch of optical glass at a time, all treated rigorously alike, in accordance with test discs or pilot discs that have been sent through first, several of the discs will turn out so different and unlike the others that the only explanation can be difference in the homogeneity of the glass itself. A smaller cause of variation in results may occur owing to differences in the methods of working and polishing the glass, for instance, the same optical glass worked by different firms may require slight differences in temperature to obtain equal results, and I have little doubt that when glasses are worked by the same firm at different times under slightly different conditions, the surface layer of the glass acquires very slightly different properties so far as its density and viscosity are concerned. I may here mention that I agree with Mr. J. W. French's theory that the surface layer of worked glass has a lower viscosity than the substance of the glass below, but whereas he ascribes a considerable difference in viscosity, my experience goes to show it is very slight and may be measured by a matter of 5° or 10° C., at temperatures ranging between 600° and 700° C. It is, in fact, just the point when the surface layer of the

glass becomes slightly viscous whilst the substance of the glass has not yet attained perceptible viscosity which one attempts to catch in platinising optically worked glass, where a permanent mirror is required.

As has already been indicated, the platinising temperatures have to be found experimentally for each kind of glass, and, indeed, for each batch of glass, and in practice test pieces have to be sent through first every time, where it is a question of good mirrors for optical purposes, to ensure that everything is all right. I can therefore give only a general indication of the temperature found suitable for different kinds of glass. With the collodion coating containing platinum salts and bismuth, as mentioned, hard crown glasses optically worked will attain a firm, permanent platinising at from 620° to 650° C.; worked plate glasses at about 680° C., unworked plate glass at 690° to 700° C., sheet glass at about 720° C., or higher, and a few experiments with worked quartz gave the somewhat surprisingly low result of 610° to 625° C.

In all cases this refers to glasses kept at the maximum temperatures named for three to five minutes. Of course, the time during which a glass is held at a particular temperature plays a rôle in the degree of viscosity reached, but, as Mr. Twyman has recently shown in his interesting paper on the "Annealing of Glass," the time is a factor which affects results far less quickly than actual increase of temperature. As illustrating this, I may mention the times it was found that a plain collodion film took to be completely volatilised :

at 600-650° C.	this took	2½	minutes.
500-550° C.	it took	4	"
450-500° C.	it took	18	"
400° C.	it took	20	"

One or two matters of practical importance follow from this. Firstly, a glass which has been raised to the necessary temperature for permanent platinising may be left in the furnace, if desired, for hours whilst cooling down without further risk arising of spoiling the flatness or the curvature of the glass, as the case may be. Secondly, if glass is merely being platinised for a loose deposit, in which case it is not raised to a temperature anywhere approaching the point where the surface attains slightly increased viscosity, then the time factor becomes negligible, or, rather, requires no attention, because the glass can be left in the furnace as long as one likes. For there is only one critical feature appertaining to the whole platinising process, and that is, so to contrive matters that optically worked surfaces, whether plane or curved, may retain their surface to the maximum degree possible. This brings us to the matter of furnaces and contrivances used.

The electric furnaces used have a flat muffle chamber about 6½ in. square and 2½ in. deep, and it is very important that they should be well insulated and lagged so that the temperature is as nearly even as possible over the whole heating surface. At first these furnaces were of the usual type, in which the heating coil is wound round the muffle or heating chamber. But in view of the fact that it is undesirable that the under surface of the glass should become *quite* as hot as the upper surface which is to be platinised, Messrs. Gallenkamp & Co., Ltd., undertook to construct for me furnaces of this description in which the heating coils are on top of the muffle chamber only. Three or four different patterns were successively constructed with improvements, as dictated by experience, and in the last furnace supplied, which has a muffle chamber 13 in. square and about 3 in. deep, the four heating

coils which are apt to burn out or go wrong from time to time are removable, and can be easily replaced without sending away the whole furnace.

A Foster pyrometer, enabling the temperature to be read to 5°C., or less, is employed, the quartz tubes containing the thermo couples being kept permanently in position inside the muffle chamber at the top.

The only other matter of importance is the removable slab on which the glass is placed during platinising. The desiderata for the slab are: (1) It must not affect the glass or be itself subject to chemical alteration, (2) it must have a *perfectly* plane surface, (3) it must retain that surface and not get warped. An *ideal* slab of this description has yet to be found, but after a number of experiments the best thing found was slabs of fused silica which were optically worked. I have had a number of such slabs in constant use for six months, or longer, which retained their optically worked plane surface perfectly. Other slabs would, after a few months' use, get slightly deformed, with consequent liability to spoil every large piece of glass supported on them for platinising. The makers of the fused silica have something to learn still in the way of producing an invariable product.

On the mode of using the furnace there is little further to be said, except that the glasses for platinising, supported on the silica plate, are put into the furnace at a somewhat lower temperature than the correct temperature they have to be taken to, which has previously been determined by trial pieces of the same glass, and that it is necessary by keeping careful watch on the pyrometer reading, and regulating the resistance, not to allow the temperature to exceed that determined on, and to shut off the current promptly a minute or so before the time for which it is decided to keep the glass at that temperature has expired. The glasses are then left in the furnace till it has cooled down, or, in the case of thin glasses of small area, of not more than 2 or $2\frac{1}{2}$ mm. thickness, they may be removed together with the silica plate almost at once. It is true that such glasses will show a certain amount of residual strain when examined in polarised light, but for most purposes for which surface mirrors are required that is of no moment, provided they retain their figure. All strain in the glass could, of course, be avoided by having annealing arrangements, as in the case of the preparation of optical glass.

A point perhaps worth referring to concerns the thickness of glasses for platinising. Whilst glass of every thickness, from thin micro-cover glass upwards, can be platinised, it is advantageous from the point of securing minimum disturbance of the surface to have the glass as thick as permissible, especially in the case of large plates. A suitable thickness for plates of 3 to 6 in. square is not less than 5 or 6 mm., or, say, $\frac{1}{4}$ in., whereas smaller discs or plates may be 3 or 4 mm. thick. It is inadvisable to go below 2 mm. thickness, even in the case of small discs of $\frac{3}{4}$ in. to 1 in. diameter, where optical flatness has to be retained. It is worth mentioning that when platinising the same kind of glass, but of different thickness, an allowance has to be made in the platinising temperature, as the surface of the thinner glasses naturally arrives more rapidly at the critical temperature.

CLEANING OF THE GLASS.

As is the case in other processes for silvering or platinising, it is quite an important matter that the glasses should first be thoroughly cleaned, and after quite a lot of experimenting the following method was resorted to. The glass is first immersed for 12 to 24 hours in 10 per cent. nitric acid, then transferred to clean spirits, or spirits and ammonia, then wiped with a *clean* cloth, and then transferred

to the electric furnace and kept for a short while at a temperature of 200°C. or 300°C., in order to volatilise all grease or impurities that can be burnt off. This method secures the cleanest and purest surfaces, and was found to be a great advance on methods relying upon chemical cleaning at ordinary temperatures only, which were always apt to lead to unexpected trouble.

Giving now the whole of the platinising process *en résumé* :—

- (1) The glass is cleaned.
- (2) It is coated with the collodion mixture.
- (3) It is placed in the electric furnace, brought to the necessary temperature for a few minutes and allowed to cool.
- (4) Permanent or semi-permanent surfaces are cleaned with spirit and ammonia and a minimum of rouge.
- (5) Where greater depth of tint is required, or fully platinised surfaces, the second, third and fourth operations are repeated.

It will be seen that the process as such is about as simple as it is possible for a process to be, and also that the method gives exceptional control as regards securing and repeating any predetermined depth of tint, which latter, of course, controls the amount of light which the platinised glass will reflect and transmit.

Any platinised or silvered glass may be judged according to

- (1) The percentage of light reflected.
- (2) " " " " transmitted.
- (3) " " " " diffused.

In a good glass Nos. 1 and 2 should account for nearly 100 per cent., and No. 3 should be a minimum.

REFLECTIVE POWER.

Now, with regard to the reflecting power of platinised glasses, although I have not been able to carry out exact measurements, it is interesting to note that the percentage of light reflected by no means increases in direct ratio to the amount of platinum in the glass surface. It appears rather that the increase for reflecting power for equal increments of platinum follows a hyperbolic curve, so that after a certain depth of tint has been reached very little increased reflecting power is obtained by going beyond.

The actual maximum of reflecting power obtainable has not been definitely ascertained, but curiously enough appears to exceed the amount given in the table of Silvanus Thompson's Optical Data, for clean platinum metal, viz., from 56 per cent. for blue light to 70 per cent. for red light.

The point of chief interest, of course, is how this compares with silvered surfaces, which have theoretically a higher reflecting capacity. The table above mentioned gives the reflecting capacity for glass mirrors backed with silver as 82½ per cent. for blue light to 87 per cent. for red light, and first surface mirrors ought therefore to exceed this—although I doubt whether in practice they do. In any case, regarding the question rather from the practical than from the theoretical point of view, silvered surface mirrors tarnish so readily that they have to be varnished, which somewhat affects their reflecting power, and even then they suffer steady and sometimes fairly rapid deterioration in use, owing to their delicacy and the difficulty of cleaning them; and that is where the platinum mirrors, with a somewhat

less theoretical maximum reflecting power to start with, but without the same liability to deterioration, come in to advantage for many purposes.

The fact that both silver and platinum show a somewhat higher reflective capacity for red than for blue light entails a very slight alteration of the colour of an object as seen in its reflected image. For all ordinary purposes this is too slight to be detrimental, but corresponding with the somewhat larger percentage difference in the case of platinum than of silver, it is a trifle more marked in the case of platinum mirrors. It can best be noticed if the observer looks at his or her own image first in a silvered mirror and then in a platinum mirror, when it will be seen that the latter imparts an appearance of slightly increased health, the image being just a shade redder.

From the rate of diminution in reflective capacity of platinum as compared with silver, as the wave length decreases from the visible red to the visible blue, it would be a not unnatural inference that photographs taken with a process camera in which a platinised surface mirror is used to reflect the image, would need a longer exposure than if a silvered surface mirror were used, because we here have to do with light of a further decreased wave length, viz., the violet and ultra-violet. That has, however, been demonstrated to be a fallacy by Mr. W. R. Grills, of Messrs. A. W. Penrose & Co., who made some careful comparative experiments with platinised mirrors and freshly silvered mirrors, for with the platinum mirror the photographs required considerably shorter exposure. Photographs were subsequently taken of a spectrum on panchromatic plates, which bore out the result mentioned. Mr. Grills ascribes this to the fact that a silvered surface absorbs the light in the region of the actinic rays to a much greater degree.

Platinised surface mirrors will, as might be expected, reflect heat rays, *i.e.*, red and ultra-red rays, well, and have in consequence been used satisfactorily for pyrometer mirrors, since they are not subject to damage by heat below that which will affect the glass itself, and may be removed and cleaned when necessary. The gold mirrors previously used for that purpose would not permit of this.

BACK-SURFACE MIRRORS.

A small point relating to surface mirrors on glass, whether silver or platinum, is that they can be used at the same time as back-surface mirrors. This, in the case of permanent mirrors which will bear handling, lends itself occasionally to curious applications. For instance, a single plano-convex lens may be platinised on the plane side, and mounted as a microscopic mirror, in place of mounting up two mirrors, one plane and one concave, as is usually the case. The convex lens with the mirror at the back of it acts just as the ordinary concave mirror does. There are probably a variety of purposes where it may be convenient, by platinising one surface only, to have the use of two mirrors of different curvatures or properties. It may be mentioned, however, that the reflecting power is not quite so great when a platinised surface is used as a back reflector as when used as a first surface mirror.

EXPERIMENTS WITH OTHER METALS.

A considerable number of experiments have been made to produce surface mirrors with metals other than platinum, by the same method as described in this paper, but no success was attained, except with other metals of the platinum group. Platinum itself gives the nearest approach to a perfectly neutral tint, and it is

interesting to note that however little platinum is either deposited on, or incorporated with, the surface layer of the glass, the tint is always a neutral grey, thus differing from the deposition of silver or gold, for example, which according to the method of deposition may start with quite a different tint from that obtained when the deposition has attained a greater depth of density. In the case of iridium surface mirrors, produced like the platinum surfaces described, the tint produced is of a more pronounced blue grey than in the case of platinum. Here also the actual hue does not suffer noticeable change according to the amount of iridium deposited. In the case of palladium a light deposit is of a yellow colour, and the maximum deposit obtainable by the burning-in process described shows a rich yellow orange colour, the hue varying in this case according to the amount of palladium introduced into the coating.

In conclusion, as I believe the present discussions are intended to further the subject of Reflecting Surfaces, not only in its scientific, but also in its more immediately practical bearings, I may perhaps be pardoned for referring to a personal matter, viz., that my firm is no longer manufacturing platinised mirrors. I only entered into optical manufacturing industry owing to the exigencies of the war, and because requested to do so, and only produced special products based on new research work. I now find that, whilst without doubt the manufacture of such special articles can be perfectly carried on by firms already engaged in the manufacture of other optical products, an establishment for carrying these on by themselves alone cannot be kept up without incurring considerable loss, as the commercial demand is not sufficiently important for this. I have therefore recently applied for patents for the new platinising process, so that those who are interested in the matter may acquire licences for working it. Without any reference to these matters, I am rather fearful of the kind of correspondence which would arise from the publication of this paper.

12.—“A NOTE ON MIRRORS FOR USE IN OPTICAL INSTRUMENTS
UNDER INDUSTRIAL CONDITIONS.”

By W. G. COLLINS.

(The Cambridge and Paul Instrument Co., Ltd.)

During the development of the Féry radiation pyrometer for industrial purposes difficulties were encountered in finding a perfectly satisfactory substance or process for the production of the concave mirror used in the instrument. In ironworks and foundries excessive dust and water vapour may be present in addition to chemical fumes, and for many purposes it has not been found practicable to protect the mirror with a glass or similar substance on account of the screening effect produced. The difficulties to be overcome were therefore of both a chemical and physical nature. The earlier mirrors were made of glass with a reflecting surface of gold, but the film of gold obtainable was so thin as to preclude the possibility of cleaning. Glass mirrors with a film of palladium were also tried, but with much the same results as with gold. Mirrors of the speculum metal type and of various compositions were also used, but under certain conditions either tarnished, or a dull film which was difficult to remove formed over the surface. Nickel alloys were then tried, and one of them (a German product), the composition of which is unknown, gave quite good results. The introduction of stainless steel prompted some experiments with it, and it appears to be the most satisfactory material obtained up to the present time.

The advantages in its favour are as follows :—

- (1) It is unbreakable under ordinary conditions of use.
- (2) It tarnishes much less readily than any of the other metal mirrors tried.
- (3) It is harder and tougher than any of the alloys mentioned and can readily be cleaned by a careful person without fear of damage to the reflecting surface, at any rate for pyrometric work.

The reflecting power of a mirror made of stainless steel was investigated at the National Physical Laboratory for white and red light (obtained with a No. 25 Wratten filter) incident at about 45° . The reflecting coefficient was found to be 68 per cent. and the variation of reflecting power with colour was negligible, viz., 0.75 per cent. more with the red.

An endeavour is being made to obtain some of the “Stellite” alloys, as these probably possess a still greater degree of hardness and not improbably an equal resistance to chemical action.

13.—“A PHOTOMETRIC METHOD OF MEASURING THE REFLECTING POWER OF MIRRORS.”

By JOHN W. T. WALSH, M.A., M.Sc.

(The National Physical Laboratory.)

The object of the present paper is to describe briefly the method used in the Photometric Department at the National Physical Laboratory for measuring the specular reflexion ratio of silvered glass mirrors. This method depends on the candle power measurement of a tungsten filament vacuum lamp of special construction, (a) with the light from the lamp illuminating the photometer screen directly, and (b) with the light suffering three reflexions on its way from the lamp to the photometer. The form of lamp used is shown in Fig. 1, from which it will be seen that the filament is of grid formation.

Three specimens of the kind of mirror under test are placed in a specially designed holder shown in Fig. 2, and from the plan (Fig. 3) it will be seen that the light is incident on each mirror at an angle of about 45 degs., and that the increase in the length of the light path due to the introduction of the mirrors is 200mm., if LA , AB , and BC are each equal to 100mm., these distances being measured in every case to the centre of the back surface of the mirror. A small blackened metal annulus is placed in front of the lamp, in order to ensure that the only light employed in the test is that coming directly from the lamp filament. The stand holding the mirrors is placed on the photometer carriage, and the lamp is then inserted independently in the central hole in the carriage, so that the plane of its filament is perpendicular to the axis of the photometer bench. The mirror holders are then in the position shown in Fig. 3a. The candle power of the lamp is measured in the usual manner, the distance between the photometer and the comparison lamp being fixed by means of a clamping rod, and the two being moved together in relation to the mirror system.

The stand to which are attached the mirror holders is then rotated into the position shown in Fig. 3b, and a second measurement of candle power is made 200mm. being added to the observed distance of the photometer head from the centre of the lamp carriage. If C_1 and C_2 be the candle powers thus found and if r be the reflexion ratio of a single mirror surface, then $C_1 = r^3 C_2$; and thus r is calculated.

In connection with this method of determination of reflexion ratio the following important considerations should be noted :—

1. The angle of incidence and reflexion of light is about 45° on the front surface of the glass. Owing to the small size of the source (approximately 20mm. square) in comparison with its distance from the photometer (generally of the order of 1,500mm.) the deviation from this mean angle will be less than $\pm 1^\circ$. It must, however, be remembered that the angle of incidence of the light on the silvered surface (taking μ for glass as 1.5) is 28° . No attempt has been made, so far, to make measurements at any other angles of incidence of the light.

2. No attempt has been made to get rid of the effect of the images formed by reflexion, internal or external, from the glass surfaces. The most important of these is that formed by reflexion of the incident light at the front surface of the mirror glass, since, with all but the thinnest glass, the other images will be so displaced by



FIG. 1.

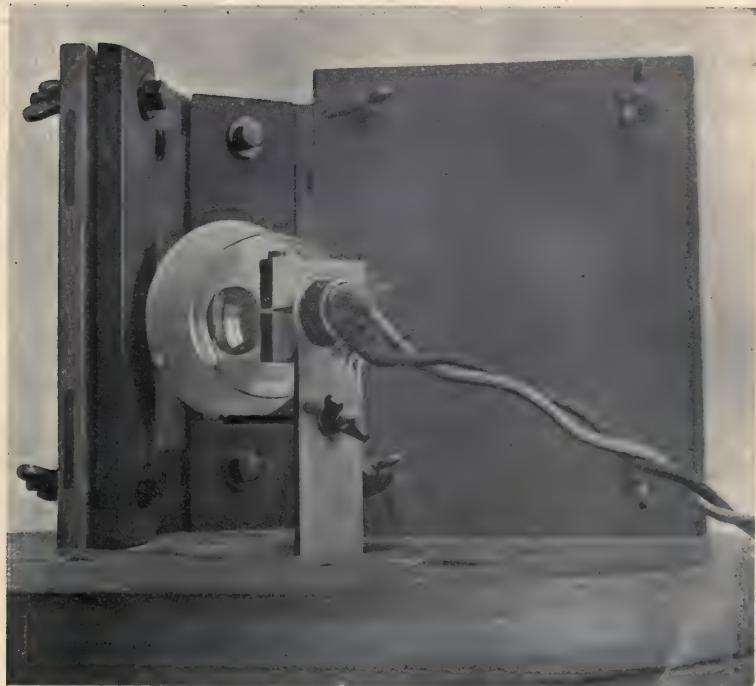


FIG. 2.

To face page 38.]

subsequent reflexions that the light from them will not reach the photometer. Since the object of the tests so far carried out has been, in the main, comparative, the elimination of this source of error, which would involve considerable complication of the apparatus, has not been undertaken. The absolute values of the reflexion ratio obtained with this apparatus must therefore be understood to include the light reflected at the front surface of the glass, as well as that reflected from the silvered back surface.

3. The reflexion ratio, measured in the way described, includes the loss of light by absorption in the material of the glass. Thus for the true comparison of different



FIG. 3a.

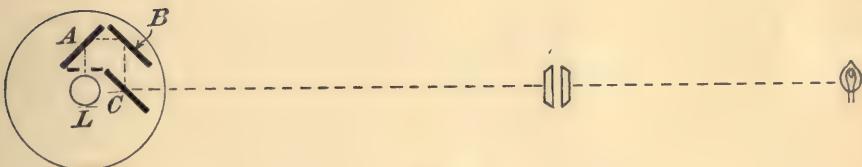


FIG. 3b.

methods of silvering, it is essential that the same thickness and quality of glass should be employed in every case. The method thus gives the value of the reflexion ratio for the mirror as a whole. The effect of absorption in the glass could, however, be easily allowed for by determining by this method the reflexion ratio of two sets of mirrors in which the glass thicknesses were different.

GENERAL DISCUSSION.

Sir FRANK DYSON: The part which interests us at Greenwich most is the silvering of large reflectors, and this is, I think, almost entirely a question of manipulation and practice. Of course, a big mirror has to be swung and kept moving and swabbed when the liquid gets muddy, and it is very largely practice and manipulative skill which make for success, and one really does not understand the chemical process very well. It is simply by experience that one finds out how to get a good surface.

I was very interested in the description of the Mount Wilson reflectors, and to hear that they could be repolished so many times. I do not think we have had anything like such a good experience as that. That they should be able to take a mirror, use it, and then polish it up again week after week, and have the mirror going for half a year seems to me very extraordinary.

Prof. F. J. CHESHIRE: In 1903 I paid a visit to the firm of Carl Zeiss at Jena; they had just installed the apparatus for making a large reflector, and were, therefore, very interested in the question of silvering. Dr. Czapski told me then that they had given a large sum of money for a secret silvering process. When they got particulars of this process they were very much dis-

appointed, because it was practically their own process, but when it was applied strictly according to the instructions it gave a result far superior to anything produced by their own processes, and therefore he thought they had made a very good bargain. Now I think that bears out once more the lesson that the operation of silvering is an art rather than a science. I have been struck by that several times here in England. I remember at one time going to look over the works of a firm that had a reputation for their silvering. I think they turned out a little better silvering than—certainly as good as—any firm in the world. I was taken into the silvering room, and I thought at last the great secret was about to be revealed. But no; the managing director told me he did not know it himself; he said: "As a matter of fact, *that* is the only man who knows all about it." That was the man who was doing the silvering.

Mr. T. SMITH: It seems to me unsatisfactory that a matter of such importance should be such an utter mystery as this question of silvering appears to be at the present time. Now that physical chemistry is attracting so much attention it is high time that someone undertook the systematic investigation of these processes and laid our knowledge on a sure foundation. I very much hope that will be done.

We have heard from Mr. French some figures relating to the reflecting power of mirrors. I must say that those figures seem to me very surprising.

Mr. H. A. HUGHES: At the beginning of the war I went into the question of silvering very carefully, but I cannot claim that I possess the art of silvering. Certainly one operator does get better results than another, and I think it all lies in the cleaning; it is the careful and clean worker who gets the best results.

A point in silvering that has interested me, especially in regard to small mirrors, is the waste of the silver solution. If we had some means of coating the surface without immersion, it would certainly effect a considerable economy. We tried fixing the mirror to the back of a plate and hanging it in the liquid. We also considered the use of the "pistol" that Commander Barnes in the Navy uses, where he mixes his two solutions in a pistol. That is no doubt a very economical method for a large surface, but I do not think it has much application to small surfaces.

There was one point which came up in the war. It was necessary to coat the surfaces of the silver with metal copper deposit, and it was certainly found that by putting two coats of the silvering deposit, giving a thick coat, you got a much more satisfactory surface of copper.

Dr. R. S. CLAY: I might just say two things. One of our students found, in experimenting with silver solutions some two years ago, that a small quantity of methyl-violet helped in producing a good film. ("Brit. Journ. Phot." Vol. LXVI., p. 155). I have never seen commercial silvering, but a friend of mine told me he managed to penetrate into the secret chamber on one occasion, during the operation of silvering ordinary plate-glass mirrors. They were silvered on a warm table, and the silvering solution was brought in what looked like a dirty jug, and was poured over the surfaces; he told me that no deposits occurred in the jug, which remained entirely clear and free from silver, so that apparently nothing happened until the liquid reached a warm glass surface.

Mr. J. W. T. WALSH: I have no experience of silvering surfaces, but I should like to hear if anyone has any experience of the process described a little while ago in an American paper—I cannot remember the name—in which the searchlight mirrors were prepared by silvering a glass mould, then coating this on the back with copper, and finally stripping the combined silver and copper surface off the glass. It was stated that the process gave extraordinarily good results, and that a single glass surface would give a large number of copper-coated mirrors, all of which showed very closely the same characteristics.

Colonel A. C. WILLIAMS: I should like to point out that in the Service some mirrors have to stand very severe usage. Take a heliograph mirror, for example. It may be sent to West Africa, where the climate is very hot and damp, and it may be in store for two or three years before being used in the sun. From experience it is found that exceedingly few mirrors will stand this without deterioration. Mirrors made by some firms stand it fairly well, but others not at all well; and what I feel is that at present there is no really satisfactory method of testing new mirrors.

I should also like to know if the composition of the glass on which the silver is deposited has any effect on the silver.

Again, in some mirrors in the Service there is a tendency for the silvering to deteriorate at its edge. In a horizon mirror, for example, the silvering is certain to start, if it starts at all, along the edge from which the razor has removed a portion of the silver.

Mr. C. W. DAVIDSON: With regard to the point about certain qualities of glass taking the silvering better, I cannot answer the question, but it does raise an interesting point which I came across in Mr. Wadsworth's paper in the "Astrophysical Journal," namely, that worked glass silvers less readily than unworked glass; that has been my own experience.

I should like to ask whether anyone knows anything of the spray process. We have had mirrors silvered by the spray process; the result is quite good, but it did not seem to be anything like as lasting as that produced by the Brashear process.

Mr. W. GAMBLE: I have been interested for a number of years in the silvering of large surfaces of glass for photographic purposes. One difficulty met with is in regard to the sugar which is used for the reducing process. We have found that pure cane sugar is the best, and the best form in which to use it is as sugar-candy—the old-fashioned sugar-candy which you used to buy in the shops. During the war we had some difficulty in getting it, and we had to get a Government permit and send to Holland for it, where it is largely used for sugaring coffee. We have found the tartaric acid process the best. Some years ago we bought a process, and, as in the case of that mentioned by Prof. Cheshire, we found it was very similar to what we had been using; but we have continued to use the new process, and we think we are getting better results, although it appeared to be the same as the old one. So it really is on the manipulation, care and cleanliness that the success of the silvering process depends.

The method of spraying-on the solutions from a double spray, so that they are supplied separately but simultaneously, was found to be quite a good procedure.

With regard to polishing mirrors, I should like to emphasise as an important point that the mirror, the pad, and the rouge should be perfectly dry and warm; in that way one is able to re-polish a mirror a good many times.

I should have liked to hear something said about the patent of Mr. Dennis Taylor on the matter of preventing tarnishing by enclosing the mirror in a hermetically sealed box, in which was contained some desiccating and absorbing medium. We have tried various methods of protecting mirrors with varnishes—a varnish called Zapon, which was obtained from Germany before the war, celluloid, &c.—and the difficulty is that if you apply the varnish thin enough you get an iridescent film which affects the definition, and if you apply it thickly it affects the brilliancy.

With regard to silvering on glass and then coppering and stripping, a good deal of work has been done, which may be found in the "Proceedings" of various scientific societies.

Mr. S. J. PACE: I have made investigations on the silvering of vacuum flasks for liquid air. The reflecting power of ordinary deposits is all right for visual rays, but very bad for other parts of the spectrum. I think I succeeded in solving the problem; I use the ordinary solutions, silver nitrate and formaldehyde, but the method of application is probably rather novel. The best method of cleaning I found was to use dilute sulphuric acid for removing grease, then to wash carefully in double-distilled water. One gets very much better results by heating the glass very nearly to redness and then soaking it well in the silvering solution before applying the reducing solution. The solution, when ready for silvering, should have an opalescent tint, and there must be silver present in colloidal form before a satisfactory metallic film can be obtained. I find, contrary to the text-books, that one gets better results by using strong solutions, and by agitating the vessel pretty violently until the silvering is completed. After adding reducing solution there should be a colour change—through various shades of orange and pink to dark yellow—and there must not be any precipitation until the film is practically complete. The first indication of a film forming should be a transparent lilac film of colloidal silver; the metallic film then forms on this. There is no doubt that one does not get anything like 98 per cent. reflecting power for infra-red radiation. The surface of the silver, if properly prepared, will keep practically free from tarnish even if exposed to the fumes of a chemical laboratory.

Mr. P. F. EVERITT: There is one point in connection with the silvering of mirrors which I have not heard raised to-night. There are two kinds of silvered mirrors. There is the mirror as used for astronomical reflectors, in which you silver the working surface and take the reflection from the silver itself. There are a good many other optical mirrors in which the silvering is, as usual, deposited on the glass, but where the working surface of the silver is under the glass. Now, it is probable that a formula that gives the best results when you are working through the glass.

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may not be the best silvering process when you are taking the reflection from the exposed silvered surface. They are very closely connected problems, but they are not the same ; and I think that in any work done on this subject that point should be borne in mind.

With regard to the glass surface being heated to a considerable temperature—I think I heard 200°C. or 300°C. mentioned—I would warn anybody who is going to carry out that part of the process that the effect of heating and cooling a piece of glass through such a range of temperature is liable to produce some permanent deformation.

Colonel A. E. LE ROSSIGNOL : Our experience in the Service has extended more to the breaking of reflectors than to the making of them, but we have had some experience of the process, mentioned by Mr. Walsh, of the stripping of the silver from the glass forming the surface. It was done for us by Commander Barnes with what someone has described as his "pistol" process, and gave a very good surface on the back of the mirror. After electro-depositing copper on the surface he placed the mirror in a warm bath, and thus secured a replica in silver of the back of the glass surface, which reproduced exactly the polish and any little defects in the glass. The difficulty then is to preserve the surface from the effect of our well-known atmosphere. The Americans have produced very large mirrors in that special way, and they claimed that they had got a varnish which would protect it. We have never been able to find one of the mirrors that had the varnish applied, and the only ones that were tried by us showed streaky deterioration of the varnish almost immediately afterwards. But we have at present one big 5-ft. mirror made by that American process, which we have used over here ; and provided it is regularly cleaned it gives very fair results. We are now trying to find some method of protecting the silver surface formed in that way, because undoubtedly for searchlight work it will have a great future.

As regards the silvering on the back of the glass, and the reference made by different people to its protection by varnish, we have had a rather curious effect within the last few days. We have been using a mirror for the reflector behind high power arcs, and the temperature has risen to practically the melting-point of the lead of the glass mirror. We were going to have it resilvered—apparently the silver was coming off—but we found when it was stripped that the surface was all pitted at the back. Sir Charles Parsons has put forward an explanation of the effect, which I think is the correct one. This particular surface was first silvered, then varnished with shellac or some kind of varnish, and finally painted ; it was not prepared in the ordinary way in which searchlight mirrors are now ; and Sir Charles Parsons explained it by saying that with the tremendous heat you have a sort of stripping action due to the paint, in the same way that frosted window glass is made ; and on examining the surface of the glass it would seem that each little small particle of paint has shrivelled up under the heat, and has detached a small piece of glass from the glass surface. It then seems necessary, in cases where heating occurs, to avoid the use of any varnish that will affect the glass surface.

Prof. A. F. C. POLLARD : The interesting discussion this evening on chemical methods suggests that if the glass surface is physically clean and the metal is in a colloidal state, satisfactory and adherent films will be formed. I venture to use the term physically clean, as distinct from chemically clean, to convey the notion that not only the glass surface but its substance to a depth commensurate with the radius of attraction of its molecules, is free from foreign matter, such as a gas.

It is a common observation that aqueous vapour, such as that contained in the breath, condenses on ordinarily clean glass surfaces in the form of minute lenses which on the whole scatter light and give a dull appearance to the surface. The late Lord Rayleigh some time ago called attention to the fact that if a blow-pipe flame be passed across such a surface, its track is made visible by breathing on the glass again when cold. The vapour now condenses on the surface of the track as a continuous film, showing interference colours while evaporating, and indicating a physically cleaner surface than that untouched by the flame. He called this appearance a "breath figure."

While silvering glass some years ago I repeated Rayleigh's experiments and found that it was easy to get good films of silver by passing a blow-pipe flame over the surface before immersion in the solution. The glass had been cleaned chemically beforehand. A freshly fractured glass surface shows the breath figure (which phenomenon does not last long) and silvers perfectly.

The tenacity of metallic films produced by cathode bombardment, viewed in light of the fact that surface-occluded gases on glass are driven out by this means, is also highly suggestive.

I would like to ask Mr. Whipple if he has ever thought of gilding or platinising the glass or quartz fibres used in the instruments made by his firm. In the past I had occasion to use that very beautiful little instrument, the Laby string-electrometer, near a nitric acid plant. The

fumes appeared to attack the silver on the fibre and apparently minute crystals of silver nitrate were formed in the course of time. The irregular outline of the fibre reduced the precision of observation.

I append a gilding recipe which I have successfully used and which appears to be the same as that mentioned by Mr. Kanthack in his bibliographical survey. In this recipe, however, coal gas is passed through one of the solutions.

GILDING RECIPE.

Make up three solutions as follow :—

- A. 10 per cent. solution of gold chloride in distilled water.
- B. 7 per cent. solution of sodium hydrate in distilled water.
- C. Two parts of alcohol through which coal gas has passed for one hour.
One part of pure glycerine.
One part of distilled water.

Clean the glass. Boil with ammonia, wash, then boil in 1 per cent. solution of Sn Cl_2 . Rinse with distilled water. Before use mix the above solutions as follows :—

Small Quantity.—Mix 5 drops of B with 3 drops of C and dilute to 4 c.cs. Add 5 drops of A and allow to stand in the dark.

Large Quantity.—Five parts of B and 1 part of C, dilute to 80 parts with distilled water, then add 5 parts of A.

Mr. R. S. WHIPPLE : In reference to Prof. Pollard's remarks, I may say that we have not tried any chemical gilding, but we tried bombardment with platinum and gold mixed, very much like the process introduced by F. B. Fawcett for the manufacture of high resistances. We were not very successful. That was some years ago, and we are seriously considering the bombardment process at the moment. Professor Einthoven and Mr. H. B. Williams of Columbia University have independently developed successful processes. There is no doubt that the film deposited by the bombardment method is much harder and more homogeneous than that deposited by the chemical process. It has also the great advantage that it is lighter.

Mr. W. R. COOPER : There is one question I should like to ask. In ordinary electro-deposition it is well known that small quantities of what are known as "addition agents" make a great difference in the deposition. They are generally of a colloidal nature, such as glycerine or gelatine. One speaker mentioned sugar candy, which is of a similar nature. I should like to know whether addition agents have been used at all in chemical deposition for the present purpose.

Mr. WHIPPLE : The Cambridge and Paul Instrument Company have also been endeavouring to overcome similar difficulties by using mirrors made of stainless steel. Here I have one of the commercial stainless steels ground and polished in the form of a concave mirror (mirror here exhibited). It lasts extraordinarily well, and you can use it under most unpleasant conditions; if tarnished it may be polished with impunity. Mr. T. Smith has been kind enough to have some experiments made at the National Physical Laboratory on the reflecting power of these rustless steel mirrors, and for white light incident at an angle of 45 degrees they reflected 68 per cent. of the light falling on them.

Mr. J. GUILD : In the Optics Department of the Laboratory we use an arrangement for measuring the reflecting powers of mirrors, which is somewhat simpler than that described by Mr. Walsh, and has some important advantages. The source of light is a 12-volt concentrated filament, gas filled lamp, such as is employed in the Lucas signalling lamp. This is mounted at the extremity of an arm about 7 inches long, which rotates about the centre of one of the standard carriages of the photometer bench. The reflecting surface, in the case of a front reflector, is mounted, with its front surface exactly above the centre of rotation, on a removable platform which is itself rotatable about the same centre. In making a measurement the mirror on its platform is removed and the lamp is swung round until it is on the centre line of the bench. The brightness at the photometer head is balanced in the ordinary way by moving a comparison lamp at the other side of the photometer. The lamp arm is then swung through any desired angle, the mirror platform is replaced and rotated until the beam of light reflected from the mirror falls on the photometer, when the brightness is again balanced by moving the comparison lamp. The

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advantages of this method are: firstly, the measurements can be made over a wide range of incidence angle; secondly, only one specimen is necessary; thirdly, the necessary adjustments are few, since, when the mirror has once been adjusted on its platform, a whole series of observations can be made, removing the mirror and platform for direct readings and replacing them for readings with reflected light, without any further adjustment; fourthly, the effective distance from the lamp to the photometer is the same in all positions, provided the reflector is mounted with its surface over the axis of rotation (this is only strictly correct for front reflections; with mirrors silvered on the back a slight correction for the optical path in the glass has to be made), so that the calculations are of the simplest character, the reflection coefficient being given by the ratio of the squares of the distances of the comparison lamp from the photometer with and without the reflector in the path of the other beam.

Dr. ROBERTS: All the papers to-night have dealt with the deposition of metal, generally silver, on glass. I believe that one of the most difficult substances on which to deposit silver by any of these processes is wax or grease, and I find myself in the very unfortunate position of wanting to deposit metal on wax, so I should be glad to know if anyone could give me any information which would help me.

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